2001

Computational Studies of Regularities in Bond Dissociation Enthalpies and Interactions of Acetylthiocholine with Solvent Molecules

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Computational Studies of Regularities in Bond Dissociation Enthalpies and Interactions of Acetylthiocholine with Solvent Molecules

(TITLE)

BY

Wencui Zheng
1976-

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

Masters of Science in Chemistry

IN THE GRADUATE SCHOOL, EASTERN ILLINOIS UNIVERSITY
CHARLESTON, ILLINOIS

2001
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Computational Studies of Regularities in Bond Dissociation Enthalpies and Interactions of Acetylthiocholine with Solvent Molecules

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Computational Studies of Regularities in Bond Dissociation Enthalpies and Interactions of Acetylthiocholine with Solvent Molecules

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July 26, 2001

Abstract

This thesis reports the results of two different research projects. One project is an evaluation of the feasibility of applying constant bond dissociation enthalpy ratios to neutral molecules for which one atom is from group 13 or group 17 and the other atom is from group 16. The other project attempts to validate the proposal that the aromatic residues lining the acetylcholinesterase (AChE) gorge will induce entry of acetylthiocholine (ATCh) into the gorge in a manner similar to that of the neural transmitter acetylcholine.

A total of thirty AB_2 and AB molecules have been examined, where A = B, Al, Ga, Cl, Br and B = O, S, Se. After obtaining the bond dissociation enthalpies of these molecules with the G2 and G2(MP2) methods, the ratios $D^0_m(AB_2)/2D^0_m(AB)$ are computed. The results show that the most stable structure for all of the group 17 systems is bent, whereas that for the group 13 systems can be linear or bent. A constant value of 0.9 was obtained for the ratios of the bond dissociation enthalpies of the group 13 molecules, although not all of the molecules have the same point group. However, even though the group 17 molecules all have the same symmetry, the ratios for these molecules are separated into two groups (1.0 and 0.6). Good agreement between the G2 and G2(MP2) data and between the calculated and experimental data is observed.

Computational calculations have located four of the five distinct ATCh conformers. Two of them are stabilized by internal C-H···S hydrogen bonds. Three are stabilized by internal C-H···O hydrogen bonds. Each conformer forms a number of stable complexes with water or benzene. The results show that the binding energy of benzene to ATCh is identical to that of water to ATCh, which suggests that the aromatic residues that line the gorge may compete with the water outside the gorge to facilitate the entry of

ATCh into the gorge, yet allow ATCh to transit to the acylation site. The essentially identical binding energies also suggest that the cation-π interaction between tryptophan and ATCh at the peripheral site of AChE should be as effective as that between tryptophan and ACh.

Dedications

I would like to dedicate this thesis to Le and my parent for their love and support that they have given to me. They are willing to share my happiness and sadness no matter where I am and whom I am going to be.

Acknowledgments

I would like to thank Dr. Carol A. Deakyne, my advisor, for her patience and guidance throughout the whole process of these two research projects. I would never forget those sleepless nights she spent in carefully examining and correcting my thesis. Without her help, I could not finish this thesis.

Table of Contents

List of Tables

Page

List of Figures

I. Introduction

A. Bond Dissociation Enthalpy Ratios

The bond dissociation enthalpy is the energy needed to separate a bond into its constituent atoms. It is one of the most frequently used energies for a molecule, since all chemical reactions involve forming and breaking bonds. With these data, it may be possible to avoid doing experiments that are fruitless and to estimate other useful data, e.g. reactivity trends.[1,2] However, there are no experimental bond dissociation enthalpy values available for many observed molecules. Thus, calculating accurate bond dissociation enthalpies as well as other fundamental energies has long been an important application of quantum chemistry.[3-5] Calculated bond dissociation enthalpies have been widely used in studies [3,6-9] in order to discover the characteristics of the chemical bonds of interest. In this project, bonds in the selected BAB and AB molecules are broken in the following ways.

$$AB \text{ ----> } A + B \qquad (1)$$

$$AB_2 \text{ ----> } A + 2B \qquad (2)$$

As reported by Curtiss and co-workers in 1991 and 1993, G2[9] and its time saving modified version G2(MP2)[10] are two reliable computational methods for obtaining thermodynamic data, especially for organic and inorganic systems with up to six or seven heavy atoms. These two methods were developed to provide accurate total energies of molecules at their equilibrium geometries. The importance and reliability of the G2 and G2(MP2) procedures have been widely accepted since their introduction. They are now frequently applied to calculate enthalpies of formation, bond dissociation enthalpies, atomization energies, proton affinities and electron affinities, with an accuracy of about

10 kJ/mol (2 kcal/mole) with respect to experiment.[9-11] Another reason the G2 and G2(MP2) methods are so popular and powerful is their ability to predict the thermochemical properties of a wide variety of systems, including unstable molecules, transition states and even novel molecules whose existence is still uncertain.

Exploring the applications of the G2 and G2(MP2) procedures to larger systems has shown that combining these procedures with a standard set of "bond separation reactions" [12], which is a set of isodesmic reactions that separate large molecules into smaller ones, can greatly reduce accumulated systematic errors and remarkably improve the accuracy of the G2 and G2(MP2) methods.[11,12-16] For example, without this combined approach the magnitudes of the errors in the enthalpies of formation calculated with the atomization method show a direct relationship with the number of formal double bonds.

Although the G2(MP2) method saves computational time and space compared to the G2 method without sacrificing accuracy, it still uses up a lot of computer resources. Curtiss et al. recently introduced the G2(MP2, SVP) method,[17-20] which is similar to G2(MP2) but reduces the calculational level from MP2/6-311G(d,p) to MP2/6-31G(d) and from QCISD(T)/6-311G(d,p) to QCISD(T)/6-31G(d). Although the G2(MP2, SVP) method is slightly less accurate[21-23], up to 80-90% of the computing time and disk storage space can be saved for the same molecular size compared to the G2(MP2)method. Thus, the G2(MP2, SVP) procedure enlarges the size of molecules that can be computed.

G2MS is another method similar to G2 that has been proposed recently.[4,24] It can handle systems of eight to ten heavy atoms. The G2MS energy can be expressed by equation *3*.

$$E(G2MS) = E[CCSD(T)/6\text{-}31G(d)] + E[MP2/6\text{-}311+G(2df,2p)] \quad (3)$$

$$- E[MP2/6\text{-}31G(d)] + HLC_{G2MS}$$

The results for a common set of molecules showed that the average absolute deviation from experimental data for this time saving method is 1.1 kcal/mol, compared to 1.0 kcal/mol for G2 and 1.2 kcal/mol for G2(MP2).

Patrick O'Hare and coworkers at the National Institute of Standards and Technology (NIST) [25] have published experimental results for the bond dissociation enthalpies of neutral BAB and AB species, where A = C, Si, Ge (in group 14) and B = O, S, Se, Te (in group 16). They have shown that there is a simple relationship between the bond dissociation enthalpies of these species, i.e. the ratio of half of the bond dissociation enthalpy of the triatomic species to that of the diatomic species ($D^0_m(AB_2)/2D^0_m(AB)$) is a nearly constant value of 0.8.

Ab initio molecular orbital calculations[26] on the bond dissociation energy ratios of the above molecular species confirmed the existence of such a nearly constant ratio. Further theoretical calculations have shown that this pattern is also observed if the atom A is extended to the ions isoelectronic to the atoms of group 14, i.e. to N^+, P^+, As^+, B^-, Al^-, and Ga^-.

Groups 13 and 17 contain important atoms such as B, Al, Cl and Br. Boron compounds have long been used as intermediates in organic synthesis and boronated biomolecules have been suggested to have important physiological activities in the human body [27-31] and laboratory animals.[32-34] Halogen compounds have been found to be strongly correlated with the "green house" effect and other atmospheric chemical phenomena. An ab initio computational study of B-H and B-C bonds [35] showed that their

first sequential bond dissociation enthalpies are larger than those for C-H and C-C bonds. The bond strengths of the B-H and B-C bonds examined were found to be nearly equal, whereas the B-F bonds examined were found to be much stronger. The bond dissociation enthalpies of B-N in twelve B-N bond-containing biomolecules[36] have been calculated and correlated with physiological activities including anti-neoplastic and anti-lipidermic behavior. The results support the authors' hypothesis that the attraction between the boron moiety and Lewis base sites on an enzyme inhibits the physiological pathway. A theoretical study of small BLi_n clusters [37] has indicated that the average B-Li bond length is 2.135 Å in BLi, 2.324 Å in BLi_2 and 2.174 Å and 2.282 Å in two isomers of BLi_3. Furthermore, the G2 and G2(MP2) B–Li bond dissociation enthalpies are essentially identical. An ab initio study of Al^+ bonding to methane, acetylene, ethene and ethane [38] has shown that the bond dissociation enthalpy values increase in the following order: Al^+-CH_4 < Al^+-C_2H_6 < Al^+-C_2H_4 < Al^+-C_2H_2. Studies of C-F, C-Br and C-Cl bonds[3,6] by different computational methods also reported excellent agreement between the experimental and calculated bond dissociation enthalpies.

Given the importance of atoms from groups 13 (B, Al, Ga) and 17 (Cl, Br), we are greatly interested in the ratios of the bond dissociation enthalpies of neutral BAB and AB systems, where A is from group 13 or group 17 and B is from group 16 (O, S, Se). Both doublet and quartet electronic states have been examined for thirty BAB and AB molecules. Both linear and nonlinear geometries have been investigated for each triatomic molecule. For each molecule, the most stable structure is determined by identifying the geometry with the lowest G2 energy. The bond dissociation enthalpies for

each set of the most stable two and three atom systems are computed and compared to each other and to the constant value of 0.8.

B. Acetylthiocholine

Acetylcholinesterase (AChE) is an efficient enzyme that is responsible for rapidly hydrolyzing the neurotransmitter acetylcholine (ACh, $(CH_3)_3NCH_2CH_2OCOCH_3^+$). Recent studies[39-43] have shown that the three-dimensioned structure of acetylcholinesterase (AChE) contains a gorge about 20 Å deep, with the active site, called the acylation site, at the base of the gorge. A number of aromatic residues line this deep gorge. They complex with acetylcholine by forming cation-π interactions and induce acetylcholine (ACh) to leave the aqueous environment outside the gorge, enter the gorge[44,45] and travel to the acylation site. Acetylcholine forms a tetrahedral intermediate after complexing with residues at the acylation site and then is hydrolyzed. Finally, acetic acid and choline are released from the AChE.

The non-covalent, cation-π interaction is formed by a cation interacting with delocalized π electron density, i. e. usually with an aromatic species. This intermolecular force plays an important role in the field of biology, including stabilizing the structures and affecting the chemical process of many biological molecules.[59-61]

Earlier studies have experimentally and theoretically confirmed the existence of cation-π interactions[62,63] between alkali metal ions and aromatic molecules. Kebarle and co-workers showed[64] in 1981 that the binding energy of $K^+(C_6H_6)$ (ΔH) is –30 kcal/mol, whereas the binding energy of $K^+(H_2O)$ is –29 kcal/mol. Additional studies[65-67] on the larger cations NH_4^+ and $N(Me)_4^+$ interacting with C_6H_6 yield binding energies similar to those with H_2O. Interactions between ACh and C_6H_6 have also been shown[39] to be of

similar strength to those between ACh and H_2O. This observation helps to rationalize why ACh enters the AChE gorge.[39,59,60,62,68]

It has been suggested[39,46] that the cation-π interactions, which are formed between the electron-rich face of the aromatic residues and the $(CH_3)_3N$— group in ACh, are strong enough to help induce acetylcholine to enter the AChE gorge but are weak enough to allow acetylcholine to reach the acylation site. In other words, the stabilization offered by the interactions between the ACh and aromatic residues inside the gorge is responsible for breaking the interactions between the ACh and water outside the gorge and for dragging ACh into the deep gorge. Once ACh reaches the acylation site, it forms interactions with polar organic and aromatic ligands.

Acetylthiocholine (ATCh, $((CH_3)_3NCH_2CH_2SCOCH_3^+)$, in which a sulfur replaces the ether oxygen in ACh, has drawn a certain amount of attention recently as a substrate of AChE because of its similarity to ACh. Studies [47-54] have shown that ATCh is rapidly hydrolyzed at the acylation site at the bottom of AChE gorge, then thiocholine and acetic acid fragments are released as the hydrolysis products. They also indicate[53] that ATCh may be an efficient competitor of ACh at the acylation site. A lot of the studies[49, 55-57] published recently on ATCh binding to AChE have been concerned with ATCh binding to the second substrate binding site (the peripheral site) of AChE. The results show that the binding of acetylthiocholine to the peripheral site accelerates the hydrolysis reaction at low concentrations of ACh or ATCh but decelerates hydrolysis at high concentrations. However, the ACh concentration is not high enough under physiological conditions for the inhibition to occur.[58] Szegletes et al.[58] suggest that the key role for the peripheral site when AChE is not saturated with substrate is to increase

the hydrolysis rate in several possible ways. First, by enlarging the enzyme surface thereby increasing the number of effective substrate encounters. Second, by allowing a larger proportion of substrate molecules to advance to the active site. Third, by optimally positioning the substrate for rapid advancement to the active site. Tryptophan is one of the key residues at the peripheral site. Since the initial binding of the substrate on the AChE catalytic pathway is proposed to be at the peripheral site,[58] and ATCh and ACh have such similar structures and reactivities, we propose that cation-π interactions also provide an important part of the impetus for the entrance of ATCh into the AChE gorge.

In this study we attempt to theoretically verify the similarity in the processes of ATCh and ACh entering the AChE gorge. Ab initio computational theory has been used to study the cluster models of ATCh, ATCh(H_2O), ATCh(C_6H_6) and ATCh(H_2O)(C_6H_6). All five conformations of ATCh have been taken into consideration. All of the species mentioned above have been optimized at the HF/6-31G(d) level and stable structures have been located. Intermolecular and intramolecular hydrogen bond lengths and bond angles have been carefully examined. MP2/6-31G(d)//HF/6-31G(d) and MP2/6-31+G(d)//HF/6-31G(d) single-point energies have been computed to determine more reliable relative stabilities and binding energies. The stable structures, hydrogen bonding interactions and relative energies of different ATCh species have been compared. Analogous ATCh and ACh systems have been compared and contrasted.

II. Methods

A. Theory Background

Computational chemistry [69] reproduces three-dimensional chemical structures and simulates chemical reactions numerically via computer. It allows one to follow the whole process of a chemical reaction without performing it experimentally.

Electronic structure theory and molecular mechanics are two major areas[69] in computational chemistry. Unlike molecular mechanics, which is based on the laws of classical physics, electronic structure theory is based on the laws of quantum mechanics, and uses the Schrödinger equation to describe the wave function of particles. Since it is not reasonable to attempt to solve the exact solution of the Schrödinger equation in most cases, mathematical approximations are utilized in order to approach the exact solution to the extent desired.

The ab initio method is one of the most popular electronic structure methods.[70,71] This method yields high quality, quantitative predictions for a wide range of systems.

1. Ab Initio Methods

The term *ab initio* means "from the beginning" [71] in Latin. It indicates that this calculational approach is based only on the fundamental principles of quantum mechanics and excludes any experimental data. The term "ab initio method" actually encompasses many different levels of calculation that are based on different combinations of a series of mathematical approximations for solving the Schrödinger equation.

2. Hartree-Fock Calculations

The most commonly used type of ab initio calculational method is Hartree-Fock theory (HF). At the Hartree-Fock calculational level a major approximation, called the

central field approximation, is made when calculating electron-electron repulsion. Without this approximation, the electron-electron repulsion calculations must be carried out between the electron of interest and all of the other electrons in the system. For example, consider an atom containing electrons *a, b, c* and *d*. When evaluating the repulsive interactions with respect to any one electron in the atom, e. g. *a*, one must calculate the repulsions between *a* and *b*, *a* and *c,* and *a* and *d*, respectively. Under the central field approximation, electron *a* is taken as the center of the system and no other individual electrons are treated explicitly. The total repulsion calculated for electron *a* neglects instantaneous electron-electron interactions, i.e. electron *a* moves in a potential for which the motions of the other electrons have been "averaged out".

In this way, the Schrödinger equation for a multiple electron system can be simplified into a series of one-electron equations that are easier to solve. In other words, a multiple electron wave function is separated into an anti-symmetrized product of one-electron wave functions, and the electron involved is the one that has been considered as the field center. The energy calculated under the central field approximation is always greater than the exact energy and will gradually approach the exact energy as corrections are made.

3. Electron Correlation Methods

Since the central field approximation gives the average effect of the electron-electron repulsion in a system, Hartree-Fock theory obviously does not provide adequate consideration of the correlation between motions of electrons, especially when two electrons have opposite spins and are not far away from each other. The two different

electron correlation methods discussed below are both extensions of Hartree-Fock theory that correct for the imprecision resulting from the central field approximation[70].

a. Configuration Interaction

The configuration interaction (CI) method recognizes that, in general, an exact wave function cannot be expressed as just one determinant, the main idea of Hartree-Fock theory. CI adds other determinants to the determinant obtained from Hartree-Fock theory by replacing one (or more) occupied orbital with a virtual orbital. The process is analogous to starting with the HF wave function and making new determinants by promoting electrons from the occupied to the unoccupied orbitals. Configuration interaction calculations can be very accurate, but require large amounts of CPU time and computer resources.

i. Full Configuration Interaction (full CI)

A configuration interaction calculation including all possible excitations is called *Full Configuration Interaction (full CI)*. Full CI calculations using an infinitely large basis set will give an exact quantum mechanical result. The wave function under the full CI method can be written as follows (equation 4).

$$\psi = b_0\psi_0 + \sum_{s>0} b_s\psi_s \qquad (4)$$

Here, Ψ_0 is the HF wave function, and in the second term, s goes through all possible substitutions. The b's are coefficients, which are set to minimize the energy of the CI wave function.

Obviously, the above equation has taken all of the possible electronic states of the particle system into consideration. All of these states have some probability to contribute and affect the total wave function.

The result of a full CI calculation is the most complete, non-relativistic solution of the Schrödinger equation. However, a full CI calculation is rarely done since it is not very practical for all but the smallest systems.

ii. Limited Configuration Interaction

Due to the time expense of full CI, a limited set of substitutions made in the Hartree-Fock wave function (truncating the full CI expression at some level) is widely used. For example, for the level of theory denoted QCISD(T), S requests inclusion of single substitutions, D requests inclusion of double substitutions, and (T) requests inclusion of triple substitutions (included perturbatively). The QCI method is different from CI in that it is not size-consistent. Terms are added to the QCI result to maintain the size consistency.

b. Møller-Plesset Perturbation Theory

An alternative approach to the electron correction problem is *Møller-Plesset Perturbation Theory*. This approach is not constructed by truncating the full CI expression, but treats the Hamiltonian in the Schrödinger equation as the sum of two parts as given below in equations 5 and 6:

$$\hat{H}\Psi = E\Psi \tag{5}$$

$$\hat{H} = \hat{H}_o + \lambda\hat{V} \tag{6}$$

where:

$\hat{H}_o$ *is the zero order term.*

$\hat{V}$ *is a small perturbation part applied to* $\hat{H}_o$.

Then, the wave function and energy can be expressed as:

$$\Psi = \Psi^{(0)} + \lambda\Psi^{(1)} + \lambda^2\Psi^{(2)} + \lambda^3\Psi^{(3)} + \cdots\cdots \quad (7)$$

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \lambda^3 E^{(3)} + \cdots\cdots \quad (8)$$

The MP2 method is the second-order Møller-Plesset Perturbation method, for which the above equations are truncated after the second term. MP3 and MP4 are the third and fourth-order Møller-Plesset Perturbation methods, respectively, whereas HF is the first order perturbation method.

The accuracy of the HF, MP2, MP4, full CI and QCISD(T) methods can be easily indicated as below:

HF < MP2 < MP4 < QCISD(T) <·····< full CI

4. Basis Sets

A basis set is a set of one-electron functions that is used to describe the shapes of the molecular orbitals in a particle system. It indicates the number and type of atomic orbitals involved in forming the molecular orbitals in the Linear Combination of Atomic Orbitals (LCAO) expansion[71]. The basis set chosen is an important factor in achieving the desired calculational accurancy within a reasonable length of time. Different calculational methods can use the same basis set and different basis sets can be used with the same calculational method. Several different types of basis sets[70] are discussed below.

a. Minimal Basis Sets

A minimal basis set comprises the minimum number of basis functions that are required to accommodate all of the electrons in the isolated atom.

For example: H: 1s

C: 1s, 2s, $2p_x$, $2p_y$, $2p_z$

b. Split-Valence Basis Sets

A double-zeta basis set is formed by doubling all of the basis functions in the minimal basis set, which allows each orbital to adjust its size in the molecular system. Likewise a triple-zeta basis corresponds to tripling the number of basis functions. Since the inner-shell electrons contribute little to chemical bonding, the double-zeta basis set can be simplified to the split-valence basis set for which only the valence shell basis functions are doubled.

For example for the split-valence basis set:

H: 1s', 1s''

C: 1s,

2s', $2p_x$', $2p_y$', $2p_z$'

2s'', $2p_x$'', $2p_y$'', $2p_z$''

c. Polarization Basis Sets

Both of the above basis sets consist of only basis functions that are centered at the nuclear positions. In other words, for all of these functions the electronic charge is symmetric about the atomic centers. However in some cases, the ability to transfer the charge center away form the nuclear position is required. For this purpose, polarization basis sets include orbitals with angular momentum quantum number ℓ beyond that required for the ground state electron configuration of the atom (e.g. d functions on heavy atoms, p functions on H and f functions on transition metals).

d. Diffuse Functions

All of the basis sets discussed so far are most suitable for molecules for which the electrons are closely held to the nuclear centers. However, for most negatively charged particle systems, molecules with lone pairs and excited molecules, the electron density is,

to some extent, far away from the nuclear centers. Thus diffuse functions are added to the basis set to make up for this deficiency .[70]

Now consider a standard basis set used in this project, the MP2/6-31+G(3df,2p) basis, for a better understanding of the concept of basis functions.

The MP2 indicates that a second order perturbation calculation is to be performed. The numbers before the dash provide information on the core orbitals. The numbers after the dash provide information on the valence orbitals. The ''6'' means that a linear combination of six gaussian functions is used to describe each core orbital. The "311" indicates that the s and p valence orbitals are tripled. The "3" means that three gaussian functions are linearly combined to describe the first valence shell. The first "1" denotes that one gaussian function is used to describe the second valence shell. The second "1" denotes that one gaussian function is used to describe the third valence shell. The "+" indicates that one diffuse s-function and one set of diffuse p-functions have been included for the non-hydrogen atoms. The term before the comma in the parentheses refers to the number and type of polarization ($\ell \geq 2$) functions added to the heavy atoms. The term after the comma refers the number and type of such functions added to the hydrogen atoms.

B. Calculational Details

1. Bond Dissociation Enthalpy Ratios

a. G2 and G2(MP2) Energies

As mentioned above, all calculational levels involve approximations that make the results deviate from the exact energy of the particle system. The Guassion 2 method

(G2)[9] has been developed to reduce this error by combining results from several of the above mentioned ab initio methods. The G2 energy is expressed by an equation that will be discussed in detail below.

The G2(MP2) approach[10] is a revised version of G2. Only MP2, rather than MP4, calculations are carried out in the G2(MP2) approach. As a result, although slightly less accurate, G2(MP2) energies require less computer time and resources.

The following steps are procedures that have to be carried out in order to determine G2 and G2(MP2) energies.

Step 1. The initial structure is input and optimized at the Hartree-Fock level using the 6-311G(d) basis set. The vibrational frequencies are also computed.

Step 2. Based on the equilibrium structure obtained from the first step, a higher level (MP2) optimization with a larger basis set 6-311G(d,p), written as (MP2/6-311G(d,p)) is performed to achieve a more accurate optimum structure and harmonic vibrational frequencies.

Step 3. After obtaining the final equilibrium geometry, the thermochemical data, i.e. zero-point-vibrational energy (ZPE), enthalpy, entropy and Gibbs free energy, are calculated.

Step 4. Single-point energies are computed at the MP2, MP4 and QCISD(T) levels with the 6-311G(d,p) basis set. These energies are output as E(QCISD(T)/6-311G(d,p)), E(MP2/6-311G(d,p) and E(MP4/6-311G(d,p)

Step 5. Single-point energies are computed at the MP2 and MP4 levels with the 6-311+G(d,p) basis set, i.e. when adding diffuse sp-functions on the nonhydrogen

atoms. These energies are output as E(MP2/6-311+G(d,p)) and E(MP4/6-311+G(d,p)).

Step 6. Single-point energies are computed at the MP2 and MP4 levels with the 6-311G(2df,p) basis set, i.e. when adding one additional set of d functions and a set of f functions to the nonhydrogen atoms. These energies are output as E(MP2/6-311G(2df,p)) and E(MP4/6-311G(2df,p)).

Step 7.The MP2/6-311+G(3df,2p)) single-point energy is calculated.

The above seven steps are specifically chosen because they yield the useful information listed below:

a. The post MP4 energy correction:

$$\Delta E(QCI) = E(QCISD(T)/6\text{-}311G(d,p)) - E(MP4/6\text{-}311G(d,p)) \quad (9)$$

b. The effect of adding diffuse sp-functions:

$$\Delta E(+) = E(MP4/6\text{-}311+G(d,p)) - E(MP4/6\text{-}311G(d,p)) \quad (10)$$

c. The energy correction for adding a second set of d polarization functions and a set of f polarization functions on the nonhydrogen atoms:

$$\Delta E(2df) = E(MP4/6\text{-}311G(2df,p)) - E(MP4/6\text{-}311G(d,p)) \quad (11)$$

d. The energy change for adding a third set of d polarization functions on the nonhydrogen atoms and a second set of p polarization functions on the hydrogens:

$$\Delta = E(MP2/6\text{-}311+G(3df,2p)) - E(MP2/6\text{-}311G(2df,p) \quad (12)$$
$$- E(MP2/6\text{-}311+G(d,p) + E(MP2/6\text{-}311G(d,p))$$

e. When these correction terms are added to the energy based on the MP4/6-311G(d,p) calculation (see the equation below), the more accurate energy

obtained is essentially equal to the energy obtained from the much more time consuming QCISD(T)/6-311+G(3df,2p) calculation.

$$E1 = E(MP4/6\text{-}311G(d,p)) + \Delta E(+) + \Delta E(2df) + \Delta E(QCI) + \Delta \quad (13)$$

f. In order to achieve as accurate results as possible, G2 and G2(MP2) theory go further to fill the gap between QCISD(T) and full CI by introducing a "higher level correction" (HLC)[9,10] into the calculation.

$$HLC = -An_{\alpha} - Bn_{\beta} \text{ (in millihartrees), where } A= 4.81, B= 0.19 \quad (14)$$

g. Energy E1 is calculated under the assumption that molecules are totally static at 0K. However, molecules still vibrate at 0K. The vibrational energy is called the zero-point energy (ZPE), and it has to be included in the total energy if we want to obtain the real energy E0.

$$E0 = E1 + ZPE \quad (15)$$

So, [71] $G2 \approx E(QCISD(T)/6\text{-}311+G(3df,2p))$ (16)

$$= E1 + HLC + ZPE$$

$$= E0 + HLC$$

$$= E(QCISD(T)/6\text{-}311G(d,p)) + E(MP4/6\text{-}311+G(d,p))$$
$$+ E(MP4/6\text{-}311G(2df,p)) - 2E(MP4/6\text{-}311G(d,p))$$
$$+ E(MP2/6\text{-}311+G(3df,2p)) - E(MP2/6\text{-}311G(2df,p))$$
$$- E(MP2/6\text{-}311+G(d,f)) + E(MP2/6\text{-}311G(d,p)) + HLC + ZPE$$

$$G2(MP2)= E(QCISD(T)/6\text{-}311G(d,p) + E(MP2/6\text{-}311+G(3df,2p)) \quad (17)$$
$$- E(MP2/6\text{-}311G(d,p)) + HLC + ZPE$$

b. Calculation of Ratios

The bond dissociation enthalpy is defined as the energy needed to break a specific chemical bond. Thus, the bond dissociation enthalpy D^0_m can be expressed by the following equations for the AB and AB_2 systems.

$$AB \text{ ----> } A + B; \tag{18}$$

$$AB_2 \text{ -----> } A + 2B; \tag{19}$$

$$D^0_m(AB2) = H(A) + 2H(B) - H(AB_2) \tag{20}$$

$$D^0_m(AB) = H(A) + H(B) - H(AB) \tag{21}$$

Then the ratio of the bond dissociation energies can be written as

$$\text{Ratio} = D^0_m(AB_2)/2D^0_m(AB) \tag{22}$$

2. Acetylthiocholine

Since acetylthiocholine is a large molecule, smaller basis sets must be chosen in order to achieve balance between calculation time and accuracy. The steps involved in carrying out the ATCh project are as follows.

Step 1. Obtain an equilibrium structure and harmoniac vibrational frequencies from a reasonable initial input structure at the HF/6-31G(d) level.

Step 2. From the equilibrium structure obtained from the first step, the final structure is determined by doing a tight optimization at the HF/6-31G(d) level, i.e. the threshold values for convergence are tightened to enhance reliability.

Step 3. Recalculate the vibrational frequencies at the HF/6-31G(d) level. Evaluate the scaled (by the usual factor of 0.8929[70]) zero point energies and thermal corrections.

Step 4. Calculate MP2/6-31G(d)//HF/6-31G(d) single-point energies.

Step 5. Calculate MP2/6-31+G(d)//HF/6-31G(d) single-point energies.

III. Results

A. Bond Dissociation Enthalpy Ratios

Bond lengths and bond angles from the equilibrium linear and nonlinear AB_2 structures, both doublet and quartet spin states, are listed in Tables 1 and 2. All molecules of interest are present in the tables, with atom A coming from either group 13 or group 17 and atom B coming from group 16. All of the AB_2 species are optimized at the MP2/6-311G(d,p) level and only the B-A-B connectivity is considered here. Table 3 reports the bond distances for both the doublet and quartet spin states of the AB species.

Table 4 shows the total energies (in hartrees) for the linear doublet, linear quartet, nonlinear doublet and nonlinear quartet states of the neutral AB_2 species at several calculational levels. Each of these energies is needed for the G2 and G2(MP2) methods. All of these energies are based on the equilibrium structures optimized at the MP2/6-311G(d,p) level. The analogous total energies for the doublet and quartet spin states of the diatomic neutral molecules are given in Table 5.

G2 and G2(MP2) energies as well as the zero-point energy (ZPE), enthalpy correction and higher level correction (HLC) are listed in Tables 6 and 7. The information for the triatomic species and diatomic species is tabulated separately.

Tables 8 and 9 present bond dissociation enthalpies for the triatomic and diatomic species, respectively. The bond dissociation enthalpies are reported for both the G2 and G2(MP2) methods in units of kJ/mol.

Finally, the bond dissociation enthalpy ratios are collected in Table 10. Ratios are included for systems with atom A from both groups 13 and 17.

B. Acetylthiocholine

Table 11 lists four backbone dihedral angles for each of the stable conformations of ATCh, ATCh(H_2O), ATCh(C_6H_6) and ATCh(C_6H_6)(H_2O) that have been located at the HF/6-31G(d) level. Each stable conformation has been assigned a combination of two letters to label the $\angle N_1C_5C_6S_7$ and $\angle C_5C_6S_7C_8$ dihedral angles, respectively. (The atomic numbering scheme is given in **Scheme 1**.). The letters *g*, *g'* and *t* represent the *gauche, gauche'* and *trans* orientations. Although four dihedral angles are included in Table 11, the $\angle N_1C_5C_6S_7$ and $\angle C_5C_6S_7C_8$ dihedral angles are the main parameters that distinguish one ATCh conformer from another. The $\angle C_4N_1C_5C_6$ and $\angle C_6S_7C_8C_{10}$ dihedral angles are both trans, i. e. essentially 180 degrees, in all conformers, as are all of the remaining backbone dihedral angles. The $\angle C_4N_1C_5C_6$ and $\angle C_6S_7C_8C_{10}$ dihedral angles have been reported to indicate the range of values obtained for the trans orientation. The dihedral angle is considered trans (t) if it is between 150 and 180 degrees or between –150 and –180 degrees. The gauche (g) arrangement is defined as an angle between 0 and 90 degrees. The gauche' (g') designation indicates the angle is between 0 and –120 degrees.

Since water or benzene can bind to ATCh at several different positions, the abbreviations *br, qa* and *qa3m* have been introduced to represent the different binding positions. When the ATCh carbonyl oxygen binds to a water hydroxyl group C=O···H-O, the water molecule forms a bridge between the carbonyl oxygen and the choline end of ATCh. In fact, the water oxygen interacts with a hydrogen atom from each of the methyl groups bound to the nitrogen or from two of the methyl groups and one of the methylene groups. An abbreviation of "br" is used to indicate that the water is in this bridged

position. The water molecule may also interact only with the quaternary amine moiety. When the water oxygen binds to three hydrogens, each of which is from a different quaternary methyl group (C-H····O-H hydrogen bonds), the position is labeled "qa3m". When the water oxygen binds to two hydrogens from quaternary methyl groups and one hydrogen from a methylene group, the position is labeled "qa". The possibility of the water hydroxyl group binding to the ATCh sulfur was examined, but the water migrated to either the "qa" or "br" position.

Two different interactions between the benzene aromatic ring and ATCh were considered in this work. The first has the electron-rich plane interacting with the three quaternary methyl groups and forming C-H····π bonds, which is also abbreviated as "qa3m". The second has the π ring interacting with two of the quaternary methyl groups and one methylene group, which is abbreviated "qa". Putting all of this together, the conformer designated "ATCh(C_6H_6)(H_2O),gg,qa,qa3m" has the ATCh molecule in the gg conformation, a benzene molecule bound to the "qa" position and a water molecule bound to the "qa3m" position.

All of the intramolecular and intermolecular hydrogen bonds in ATCh and its complexes are reported in Table 12. Columns two and three give the intramolecular hydrogen bond lengths and bond angles involving the *S* atom and atom H_{13} from one of the methyl groups on the choline end of ATCh (refer to the numbering sequence in Scheme 1). The last four columns present the same information for the intramolecular or intermolecular hydrogen bonds between the carbonyl *O* and a *H* (columns four and five) or the water *O* and a *H* (columns six and seven). The latter data appear only when the

ATCh complex includes a water molecule. The number within the parentheses indicates the specific H atom that interacts with the oxygen.

Table 13 presents the unscaled HF/6-31G(d), MP2/6-31G(d) and MP2/6-31+G(d) energies at 0 K and the HF/6-31G(d) zero-point energies (ZPE). The HF/6-31G(d) entropies and correction terms needed to convert the HF and MP2 energies at 0 K to energies, enthalpies and Gibbs free energies at 298 K are given in Table 14. All of the values except those for the entropy are in hartrees; the entropy values are in J/mol·K. The corresponding energies and correction terms for water and benzene are also reported in the last two rows of the tables.

Table 15 lists the scaled HF energies, enthalpies, Gibbs free energies and entropies at 298 K for all molecules examined. The corresponding data for the MP2/6-31G(d) and MP2/6-31+G(d) calculational levels are reported in Tables 16 and 17, respectively.

In order to evaluate the relative stabilities of the various conformers, relative thermodynamic data are given in Tables 18-20. Each stable ATCh conformation is compared, as is each stable ATCh(H_2O), ATCh(C_6H_6) and ATCh(C_6H_6)(H_2O) complex.

The thermochemical values for the association reactions of ATCh complexing with water, ATCh(C_6H_6) complexing with water, ATCh complexing with benzene and ATCh(H_2O) complexing with benzene at the HF/6-31G(d), MP2/6-31G(d) and MP2/6-31+G(d) levels are presented in Tables 21-23, respectively. The data have been calculated only for the most stable form of the complex at the specified calculational level (see Tables 18-20).

Figure 1- 4 show optimum structures of all the ATCh and ATCh complexes.

IV. Discussion

A. Bond Dissociation Enthalpy Ratios

1. Structures of AB_2 Species

Optimized at the MP2/6-311G(d,p) level, stable linear structures for the doublet AB_2 species with A from both group 13 and group 17 are listed in columns 2-4 in Table 1. All of these structures were forced to be linear. Stable linear structures have been located for all group 13 systems except AlO_2. For the group 17 systems, stable linear structures were found for doublet ClO_2 and $ClSe_2$. If there is no entry for a particular molecule, an imaginary frequency was observed for that structure, i.e. the structure is unstable. There is an obvious trend in the A–B bond lengths with respect to changes in atomic radii; that is, holding the A atom in the AB_2 species unchanged, the larger the B atom the longer the A–B bond length. Likewise, holding the B atom unchanged, the larger the A atom the longer the A–B bond length. For example, for the Al systems the bond lengths follow the order Al-O < Al-S < Al-Se. Similarly, for the oxygen systems the trend in bond lengths is B-O < Al-O < Ga-O.

Just a few stable linear structures were found for the quartet (excited) spin state. The trend in bond lengths is similar to that observed for the doublet (ground) state. However, the bond lengths are longer for the quartet state species than for the corresponding species in the doublet state, since an electron is promoted into a degenerate antibonding orbital increasing the antibonding character of the molecules and lengthening the bonds.

The optimized structures of the nonlinear AB_2 species collected in Table 2 indicate that stable doublet structures are still more prevalent than stable quartet

structures for both the group 13 and group 17 molecules. For each group 17 molecule, the minimum on the doublet potential energy surface has C_{2v} symmetry and a bond angle between 117 and 119 degrees. Bond lengthening is still observed as either the A or B atom goes down the periodic table for both the doublet and quartet spin states. The equilibrium structures of the diatomic species given in Table 3 show a similar bond length trend.

2. Relative Stabilities

In Table 4 the MP2, MP4 and QCISD(T) single-point energies of the triatomic species calculated with different basis sets have not yet been modified with the corresponding zero-point energy. Nevertheless with the exception of ClO_2, for each of the molecules considered, each of these single-point energies predicts the same ground state structure as do the G2 and G2(MP2) energies in Table 6. That is, regardless of the calculational level, each of these triatomic and diatomic molecules (Tables 4 and 5) are predicted to have doublet ground states (lowest or most negative energy). In addition, the most stable structure for all of the group 17 systems is bent, whereas that for the group 13 systems can be linear or bent.

The energies in Tables 4 and 5 also indicate that increasing the size of the basis set results in more accurate energies. For example, examining the MP2 energies for the BO_2 linear doublet structure, energies 0.008 hartrees closer to the G2 energies (Table 6) are obtained by expanding the basis set from 6-311G(d,p) to 6-311+G(d,p). Similar results are observed when the basis set is expanded from 6-311+G(d,p) to 6-311G(2df,p) and then to 6-311G(3df,2p). When using the same basis set, more accurate energies result from including more perturbation terms, e.g. the MP4 energies are closer to the G2

energies than are the MP2 energies. Similar patterns can be seen for the energies of the diatomic molecules in Table 5.

Since elements in the same group with the same electronic state have the same number of α and β electrons, the higher level corrections (HLC) in Table 6 are identical for all of the group 13 molecules. The same is true for all of the group 17 molecules and the molecules in Table 7.

Compared with the G2 energies, the G2(MP2) energies are just slightly higher, by around 0.01 hartree. This result, combined with the other results discussed below, confirms the reliability of the time-saving G2(MP2) process.

3. Bond Dissociation Enthalpies

Once the most stable structure for a molecule has been determined, this structure is used to compute the bond dissociation energy for the molecule. Since the bond dissociation enthalpy at 298 K is desired, the G2 and G2(MP2) energies at 0 K (equations 16 and 17) must be converted to enthalpies at 298 K. Therefore, for the diatomic and triatomic molecules, the G2 enthalpy at 298 K is equal to the G2 energy at 0 K plus the enthalpy correction minus the zero-point energy. Thus, H(298 K) = G2(0 K) + enthalpy correction – ZPE. Subtracting out the ZPE is necessary because it is included in both the G2 energy at 0 K and the enthalpy correction term. For atoms, the enthalpy at 298 K is calculated by the equation: H(298K) = G2(0 K) + 5/2 * RT. Here, 1.5 RT are needed to account for the translational energy difference at 0 K and 298 K, and RT is needed to convert energy to enthalpy. Similar equations are utilized to obtain G2(MP2) enthalpies. Finally, bond dissociation enthalpies are computed according to equations 20 and 21.

Note from Tables 8 and 9 that the bond dissociation enthalpy for a given triatomic molecule is less than twice that for the corresponding diatomic molecule. This result is expected since, qualitatively at least, the strength of a double bond can be considered to be about two-thirds that of a triple bond.

There is reasonably good agreement between the G2 and G2(MP2) bond dissociation enthalpies. The G2 and G2(MP2) values differ by at most 17 kJ/mol, with generally larger differences for the group 17 molecules than for the group 13 molecules. For the limited experimental data, the calculated and experimental bond dissociation enthalpies agree reasonably well for the oxygen compounds. The largest deviation in the calculated and experimental values is 20 kJ/mol, and the G2(MP2) data are in better agreement with the experimental data than are the G2 data. Unfortunately, the agreement between the calculated and experimental data is much poorer for the sulfur compounds, with discrepancies of as much as 45 kJ/mol.

4. Bond Dissociation Enthalpy Ratios

Even though there are differences between the G2 and G2(MP2) bond dissociation enthalpies, the ratios of the bond dissociation enthalpies agree with each other quite well. With the exception of the BO_2/BO system, a nearly constant ratio of 0.9 is observed for the group 13 systems. This average ratio is numerically equal to that found by Xu[26] in his study of the analogous group 13 anions. Recall that the most stable structures for the group 13 triatomics do not all have the same point group. For example, AlO_2 is C_{2v} and GaS_2 is $C_{\infty v}$. Despite the fact that the molecules belong to different point groups, the bond dissociation enthalpy ratios are nearly identical. However for the molecules with an A atom from group 17, although the most stable structures all have the

same symmetry the ratios separate into two groups, those with a value of about 1.0 and those with a value of about 0.6. Note the excellent agreement between the experimental and calculated ratio for the ClO_2/ClO system. At this point, the group 17 systems are the only systems our group has explored for which the ratios are not nearly constant (this work and reference 26). The following work has been done in order to explore the possible reasons for this result. In order to verify that the most stable geometry has been identified for the triatomic molecules, three different initial molecular bond angles (100, 130 and 160 degrees) have been tried for all of the molecules. In each case the three starting geometries optimized to essentially the same structure (Table 2). There is the possibility that these molecules are cyclic, and a starting molecular bond angle of 60° still has to be checked. However, at this point, there is no evidence to say that the ratios of the bond dissociation enthalpies are constant for the molecules from group 17, i. e. the phenomenon of having constant ratio is not observed for these systems.

5. Future Work

One possible way to improve the results for these systems would be to carry out G3 calculations for them. The G3 method[73] is the latest of the methods proposed by Pople and coworkers for obtaining reliable thermochemical data. G3 theory uses larger basis sets than G2 theory and includes a spin-orbit correction term, a higher level correction term, and a core correction term for all atoms. Since all of these systems have doublet ground states and all of the energies calculated in this work are based on single determinant wave functions, a multideterminant approach would provide improved bond dissociation enthalpies and ratios if more than one electronic configuration contributes significantly to the molecular wave function.

B. Acetylthiocholine

1. Structures of ATCh and Complexes

Four stable conformations of ATCh have been identified in this project (Table 11). According to our labeling scheme for the $\angle N_1C_5C_6S_7$ and $\angle C_5C_6S_7C_8$ dihedral angles, the four stable conformations are gg', gg, tg and tt and are illustrated in Figure 1.

For most of the arrangements we studied, binding either water or benzene to ATCh has little effect on the backbone of ATCh. Thus, when water or benzene is attached at the "qa" or "qa3m" position, no obvious changes in the ATCh backbone dihedral angles are observed. Furthermore, if water is bound to the "qa" position and benzene is bound to the "qa3m" position, switching the positions of the two ligands essentially does not affect the dihedral angles of ATCh (compare ATCh(C_6H_6)(H_2O),gg,qa,qa3m with ATCh(C_6H_6)(H_2O),gg,qa3m,qa). In other words, the external solvation of ATCh by water or benzene in these positions has only a minor effect on the internal solvation of ATCh. In contrast, when the water molecule bridges between the carbonyl group and choline end, the situation is so different that obvious changes in the dihedral angles are observed for four of the ATCh conformations. The structures of the different ATCh conformations play a major role in the reorientation of the dihedral angles. For example, in order to fit a water bridge between the carbonyl and quaternary amine groups in the gg' conformation, ATCh reorients itself by opening up the two dihedral angles $\angle N_1C_5C_6S_7$ and $\angle C_5C_6S_7C_8$ by about 15 degrees. The $\angle N_1C_5C_6S_7$ angle increases from 83 to 98 degrees, and the $\angle C_5C_6S_7C_8$ angle increases from –108 to –122 degrees (see Figure 1). For the gg conformation, the dihedral angles are too large to fit in

a water bridge; therefore, the above two dihedral angles decrease 19 degrees and 5 degrees, respectively. No angle changes are required for the fully staggered tt conformation to fit in a bridged water molecule.

Most of the differences in the analogous ATCh and ACh dihedral angles are within 5-6 degrees, but the largest difference is about 15 degrees[39]. The general trend is that the $\angle N_1C_5C_6S_7$ angle is larger and the $\angle C_5C_6S_7C_8$ angle is slightly smaller for ATCh. By replacing the ACh ester oxygen atom with a sulfur atom, the larger atomic radius and longer S-X bonds yield a longer backbone chain, which at least partially accounts for the observed differences in dihedral angles. Another result of the longer chain is that the ATCh(H_2O),gg' br complex is stable, whereas the ACh(H_2O),gg',br complex rotates to the gt conformation[39]. However, replacing the oxygen atom has a different effect on the ATCh, gt conformer. This conformer is unstable and rotates to either the gg' or gg conformer. ATCh is stable in the gt conformation only when it has a water molecule bound to it. In contrast, the ACh, gt conformation is the third-most stable of the five existing ACh[39] conformations and is the most stable conformation when ACh is complexed with water.

2. Hydrogen Bonding

The intramolecular and intermolecular interactions that meet the criteria as hydrogen bonds are listed in Table 12. C-H····O interactions are taken as hydrogen bonds if the distance between H and O is within 2.8 Å and the C-H····O bond angle is not less than 90 degrees[39,74]. The corresponding critical standards for C-H····S interactions is that the distance is within 3.2 Å and the bond angle is not less than 90 degrees. Columns two through four in Table 12 give the bond distances and bond angles for the two types of

intramolecular hydrogen bonds found in ATCh and its complexes. The corresponding information for the intermolecular hydrogen bonds involving water is tabulated in columns five and six.

For ATCh itself, C-H····S hydrogen bonds are observed for the gg' and gg conformations, with a distance of about 2.96 Å between S and H. For the complexes with ATCh in the gg' conformation, all of the C-H····S bonds have similar lengths and angles except for ATCh(H_2O),gg',br. A similar trend is seen when ATCh has the gg conformation. The changes in bond distances and bond angles observed for the "br" geometries are due to the structural changes required to fit in the water molecule.

Every structure with the gg' conformation of ATCh also has two or three C-H····O=C intramolecular hydrogen bonds involving two CH_3 hydrogens and one CH_2 hydrogen. O····H bonds involving the same hydrogen atom have similar distances and angles from complex to complex. Two of these hydrogen bonds are also observed in all of the gg and tg structures except the gg structures with a bridged water molecule. The latter complexes contain only one such interaction. When ATCh is in the gg or tg conformation, the hydrogens involved in the C-H····O=C bonds are primarily from the CH_2 groups.

In summary, the gg and gg' conformers of ATCh and the complexes involving these conformers are stabilized by a combination of C-H····S and C-H····O=C interactions. The tg conformer of ATCh and the complexes involving this conformer are stabilized by C-H····O=C interactions. In general, there are no intramolecular interactions in the tt conformer of ATCh or its complexes. Similar results were obtained for ACh.[39] However, as noted above, the gt conformer is stable for ACh but not for ATCh. The only

intramolecular interaction that stabilizes ACh,gt is a C-H····O bond to the ester oxygen. The H····O distance of 2.309 Å is shorter by 0.1 to 0.2 Å than it is in ACh,gg' and ACh,gg and the C-H····O bond angle is larger and therefore more favorable. Apparently the analogous, weaker C-H····S interaction in ATCh is not strong enough to stabilize the ATCh,gt conformer without a water present, even though the H····S distances in the ATCh,gt,qa complexes are also shorter by 0.1 to 0.2 Å.

Comparing the C-H····O=C intramolecular hydrogen bonds in ATCh with those in ACh[39] suggests that the interactions are weaker in the ATCh gg' and gg systems, since the bond lengths are generally longer but the bond angles differ little for those systems. On the other hand, the shorter intramolecular bond lengths and larger intramolecular bond angles in the ATCh tg systems suggest that the interactions are stronger for these systems than for the ACh systems. In addition, ATCh,tg and most of its complexes have one more intramolecular hydrogen bond than the corresponding ACh systems. Since the S····H interactions in ATCh will also be weaker than the O····H interactions with the ester oxygen in ACh, there may be some rearrangement of the stabilities of ATCh and its complexes compared to ACh and its complexes.

3. Relative Energies

The total energies, enthalpies, and free energies given in Tables 13-17 and the relative thermochemical data given in Tables 18-20 show that taking electron correlation into account does affect the relative stabilities of the ATCh conformers and the complexes derived from them. Expanding the basis set from 6-31G(d) to 6-31+G(d) also affects the relative stabilites but to a much smaller extent. For all of the ions examined in this work, the relative total energies are essentially equal to the relative enthalpies. The

complexes with the gg' conformer of ATCh have a lower entropy, as do the more rigid complexes containing a bridged water. Similarly to what was observed for ACh,[39] the range of entropies is sufficiently large that the trends in relative free energies are different from the trends in relative enthalpies.

All of the systems containing the tg conformation of ATCh have the lowest energies, enthalpies and Gibbs free energies; therefore they are more stable than the other systems. Using the MP2/6-31G(d) data in Table 19 (so that comparisons can be made with the ACh data[39]), the relative enthalpies of ATCh,tg and ATCh,tt indicate that the ATCh,tg conformer is stabilized by 21 kJ/mol by the intramolecular hydrogen bonds. The other two conformers are stabilized by 17 and 8 kJ/mol. Although the combined strength of the intramolecular interactions is about the same for ATCh,gg' and ACh,gg', it is twice as large for ATCh,tg as for ACh,tg and half as large for ATCh,gg and ACh,gg. As a result, the relative stabilities of the various conformations of ATCh follow the order tg > gg' > gg > tt, whereas those for ACh follow the order gg' > gg > gt > tg > tt.

Changing the position of the complexing agent from "qa" to "qa3m" affects the energy only slightly, as does switching the positions of water and benzene in the ATCh(C_6H_6)(H_2O) ions (Tables 18-20). In fact, the main effect of adding diffuse functions to the basis set is to reverse the stabilities of ATCh(H_2O),tg,qa and ATCh(H_2O),tg,qa3m, which is obviously due to the extremely similar stabilities of these two complexes. ATCh(H_2O),tg,qa is the most stable water complex with the diffuse functions (Table 20) whereas ATCh(H_2O),tg,qa3m is the most stable water complex without it (Tables 17 and 18).

It has been reported[39] recently that complexes with two waters bound to the gt conformation of ACh have the most negative free energies, in agreement with the experimental result[75] that the gt conformation of ACh predominates in aqueous solution. Also, the addition of the second water was important in obtaining this result, since with just one water ligand the ACh(H_2O),gg,qa complex had the most negative free energy.[39] and more complexing ligands more stable. It is possible that adding additional water molecules to ATCh, especially in the doubly-bridged position will stabilize the gt conformation relative to the other conformations. However, the enthalpies and free energies of the gt complexes are so unstable compared to those of the tg complexes, it seems unlikely that the gt conformation of ATCh will predominate in aqueous solution.

Useful information can be obtained from the relative energies about the influence of the intramolecular hydrogen bonds within ATCh on the intermolecular hydrogen bonds with a complexing ligand. One way to determine this information is to compare the relative enthalpies of the ions with the ACh, tt form to those of the ions with the other forms. For example, the enthalpy difference is 21.2 kJ/mol (Table 19, MP2/6-31G(d)//HF/6-31G(d) data) between ATCh, tg and ATCh, tt and 19.7 kJ/mol between ATCh(H_2O), tg, qa3m and ATCh(H_2O),tt,qa3m. Values of 16.9 kJ/mol and 14.4 kJ/mol are found for ATCh,tt and ATCh,gg' vs. ATCh(C_6H_6),tt,qa and ATCh(C_6H_6),gg',qa. Similar data are obtained for the other ions. Therefore, we can conclude that if the difference in internal structure affects the external complexing the effect is small, as it is for the ACh[39] systems.

4. Thermochemistry of Association Reactions

Compared to the HF/6-31G(d) enthalpies and free energies for the association reactions, the MP2/6-31G(d) and MP2/6-31+G(d) data are more negative (Tables 20-22). The primary effect of enlarging the basis set is to stabilize the interaction between benzene and ATCh with respect to that between water and ATCh. In fact, the difference in the reaction enthalpies for adding a water molecule and adding a benzene molecule decreases from 15 kJ/mol in Table 21 to 0 kJ/mol in Table 23. The experimental values of $\Delta H°$ for the association reactions of H_2O and $C_6H_5CH_3$ to ACh are 33.5 and 33.9 kJ/mol.[39] Since the MP2/6-31G(d) $\Delta H°$ values for the association reactions involving ATCh are within 2 kJ/mol of the calculated values for the reactions involving ACh,[39] it is likely that that the binding energies of these ligands to ATCh should also be essentially equal. Thus, employing higher level calculations and extending the basis set yields more accurate values. Furthermore, these results support our suggestion that the cation-π interaction between tryptophan and ATCh at the peripheral site of AChE should be as effective as that between tryptophan and ACh. Although the calculations involve just one or two ligands and do not take bulk effects into account, the relative binding energies in this work also suggest that the aromatic residues in the AChE gorge can effectively compete with the aqueous environment to allow entry into the gorge and transit to the active site.

Including diffuse functions in the basis set leads to better agreement between the experimental and calculated trends in the thermochemical data. Nevertheless, the theoretical reaction enthalpies are overestimated for both ligands because basis set

superposition error (BSSE) has not been taken into account. In addition, these basis sets tend to overestimate the electrostatic component of the interaction energy.

The binding energies of water and benzene to the choline end of ATCh given in Tables 21-23 show only small differences between adding the same ligand molecule to ATCh itself and to an ATCh complex. These small differences support the suggestion by Harel *et al.*[42] that the individual contributions made by the various AChE/ATCh interactions to the free energy of stabilization of the acylation transition state are additive. The result that the binding energy of water to ATCh(C_6H_6),tg,qa *is* smaller than that of water to ATCh,tg does suggest, however, another role for the aromatic residues that line the AChE gorge. Since only three water molecules are believed to be present at the active site of AChE, the aromatic residues may facilitate the stripping of water from the substrate as it leaves the aqueous environment and enters the enzyme.

V. Conclusions

A. Bond Dissociation Enthalpy Ratios

The stable equilibrium structures of doublet and quartet spin states of linear and nonlinear AB_2 and AB systems are optimized at MP2/6-311G(d,p) level, where A = B, Al, Ga, Cl, Br and B = O, S, Se. Based on these equilibrium structures, total energies and correction terms are computed to achieve the bond dissociation enthalpies D^{o}_{m} by G2 and G2(MP2) processes. The ratio of the bond dissociation enthalpies are resulted by the expression $D^{o}_{m}(AB_2)/2\ D^{o}_{m}(AB)$. A constant value of 0.9 was obtained for the bond dissociation enthalpy ratios $D^{0}_{m}(AB_2)/2D^{0}_{m}(AB)$ for the group 13 molecules, but the ratios are split into two disparate values for the group 17 molecules. The ratios appear to be independent of variations in point group and equilibrium bond angle. There is good agreement between the G2 and G2(MP2) data and between the calculated and experimental data.

B. Acetylthiocholine

Based on the result of HF/6-31G(d) calculations, three of the four ATCh conformers located are stabilized by intramolecular hydrogen bonding. Each conformation forms a number of stable complexes with water and benzene. Internal interactions in the ATCh conformers do not affect external solvation. Enthalpies of association reactions computed at HF/6-31G(d), MP2/6-31G(d) and MP2/6-31+G(d) report the binding energies of water and benzene molecules to ATCh. The essentially identical binding energies show that although there are several differences between the structures of ATCh and ACh, the aromatic residues lining the AChE gorge will aid

ATCh, as well as ACh, in leaving the aqueous environment outside the gorge. Therefore, the results of this work support the experimental observation[47-54] that ATCh is an effective substitute for ACh with respect to entry into the AChE gorge and hydrolysis at the acylation active site.

VI. References

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Table 1. MP2/6-311G(d) Geometries for Linear AB_2 Species[a,b]

Species	Linear					
	doublet			quartet		
	AB_1	AB_2	$\angle B_1AB_2$[c]	AB_1	AB_2	$\angle B_1AB_2$
BO_2	1.338	1.217	180	1.371	1.371	180
BS_2	1.728	1.612	180			
BSe_2	1.808	1.808	180			
AlO_2						
AlS_2	2.037	2.037	180			
$AlSe_2$	2.174	2.174	180			
GaO_2	1.787	1.647	180	1.835	1.770	180
GaS_2	2.014	2.160	180			
$GaSe_2$	2.142	2.293	180	2.340	2.340	180
ClO_2	1.763	1.658	180	1.679	1.679	180
ClS_2						
$ClSe_2$	2.217	2.685	180			
BrO_2				1.785	1.785	180
BrS_2						
$BrSe_2$				2.456	2.456	180

[a] Bond lengths in Å, bond angles in degrees.
[b] If there is no entry, a stable geometrical arrangement was not found.
[c] Forced to be linear.

Table 2. MP2/6-311G(d) Geometries for Nonlinear AB_2 Species[a,b]

Species	nonlinear					
	doublet			quartet		
	AB_1	AB_2	$\angle B_1AB_2$[c]	AB_1	AB_2	$\angle B_1AB_2$
BO_2	1.315	1.197	158.6	1.394	1.350	110.1
BS_2	1.649	1.649	154.3			
BSe_2	1.774	1.774	135.9			
AlO_2	1.609	1.609	152.9	1.721	1.721	150.1
AlS_2	2.014	2.054	160.4			
$AlSe_2$	2.135	2.286	155.6	2.333	2.333	153.1
GaO_2				1.740	1.740	128.9
GaS_2	2.014	2.151	159.8	2.194	2.194	156.8
$GaSe_2$	2.142	2.283	156.3	2.332	2.332	153.1
ClO_2	1.508	1.508	119.1	3.815	1.607	119.3
ClS_2	2.022	2.022	119.2			
$ClSe_2$	2.184	2.184	118.7			
BrO_2	1.656	1.656	117.4	1.774	1.774	164.4
BrS_2	2.139	2.139	116.7			
$BrSe_2$	2.291	2.291	117.2	2.452	2.452	157.8

[a] Bond length in Å, bond angles in degrees.
[b] If there is no entry, a stable geometrical arrangement was not found.
[c] Forced to be nonlinear.

Table 3. MP2/6-311G(d) Geometries for AB Species [a]

	doublet	quartet
Species	AB	AB
BO	1.208	1.367
BS	1.612	1.768
Bse	1.746	1.975
AlO	1.644	1.717
AlS	2.024	2.185
AlSe	2.155	2.408
GaO	1.708	1.879
GaS	2.042	2.319
GaSe	2.175	2.431
ClO	1.607	2.786
ClS	2.012	2.440
ClSe	2.154	2.509
BrO	1.748	2.967
BrS	2.158	2.565
BrSe	2.292	2.640

[a] Bond lengths in Å.

Table 4. Energies for Triatomic Neutral Molecules[a,b]

Species	Calculational Level	linear		nonlinear	
		E(T) doublet	E(T) quartet	E(T) doublet	E(T) quartet
BO_2	MP2/6-311G(d,p)	-174.906095	-174.590496	-174.898127	-174.723260
	MP4/6-311G(d,p)	-174.936859	-174.643983	-174.929269	-174.760521
	QCISD(T)/6-311G(d,p)	-174.939203	-174.650407	-174.932763	-174.777851
	MP2/6-311+G(d,p)	-174.913935	-174.598091	-174.905709	-174.731234
	MP4/6-311+G(d,p)	-174.944688	-174.652445	-174.936869	-174.769041
	MP2/6-311G(2df,p)	-174.992988	-174.673023	-174.984912	-174.805954
	MP4/6-311G(2df,p)	-175.028501	-174.732202	-175.020843	-174.848589
	MP2/6-311+G(3df,2p)	-175.006755	-174.686144	-174.998989	-174.820243
BS_2	MP2/6-311G(d,p)	-820.097085		-820.089176	
	MP4/6-311G(d,p)	-820.143572		-820.136344	
	QCISD(T)/6-311G(d,p)	-820.148734		-820.144122	
	MP2/6-311+G(d,p)	-820.101133		-820.093131	
	MP4/6-311+G(d,p)	-820.148089		-820.140766	
	MP2/6-311G(2df,p)	-820.187525		-820.178776	
	MP4/6-311G(2df,p)	-820.247004		-820.239116	
	MP2/6-311+G(3df,2p)	-820.195740		-820.187332	
BSe_2	MP2/6-311G(d,p)	-4824.508705		-4824.588319	
	MP4/6-311G(d,p)	-4824.556118		-4824.632753	
	QCISD(T)/6-311G(d,p)	-4824.554390		-4824.642423	
	MP2/6-311+G(d,p)	-4824.510218		-4824.589849	
	MP4/6-311+G(d,p)	-4824.557865		-4824.634505	
	MP2/6-311G(2df,p)	-4824.574330		-4824.651096	
	MP4/6-311G(2df,p)	-4824.630547		-4824.704585	
	MP2/6-311+G(3df,2p)	-4824.591862		-4824.668678	
AlO_2	MP2/6-311G(d,p)			-391.979232	-391.853328
	MP4/6-311G(d,p)			-392.017400	-391.883856
	QCISD(T)/6-311G(d,p)			-392.077614	-391.888373
	MP2/6-311+G(d,p)			-391.995568	-391.867527
	MP4/6-311+G(d,p)			-392.034293	-391.898857
	MP2/6-311G(2df,p)			-392.080076	-391.950379
	MP4/6-311G(2df,p)			-392.124085	-391.987573
	MP2/6-311+G(3df,2p)			-392.096746	-391.965527
AlS_2	MP2/6-311G(d,p)	-1037.251123		-1037.304323	
	MP4/6-311G(d,p)	-1037.296632		-1037.347277	
	QCISD(T)/6-311G(d,p)	-1037.302193		-1037.354776	
	MP2/6-311+G(d,p)	-1037.254315		-1037.308311	
	MP4/6-311+G(d,p)	-1037.300245		-1037.351610	
	MP2/6-311G(2df,p)	-1037.357795		-1037.406292	
	MP4/6-311G(2df,p)	-1037.416959		-1037.462707	
	MP2/6-311+G(3df,2p)	-1037.365917		-1037.414965	

Table 4. (cont'd.)

Species	Calculational Level	linear		nonlinear	
		E(T) doublet	E(T) quartet	E(T) doublet	E(T) quartet
$AlSe_2$	MP2/6-311G(d,p)	-5041.795020		-5041.852009	-5041.752072
	MP4/6-311G(d,p)	-5041.836557		-5041.891630	-5041.804561
	QCISD(T)/6-311G(d,p)	-5041.840951		-5041.896111	-5041.816917
	MP2/6-311+G(d,p)	-5041.796125		-5041.853360	-5041.753979
	MP4/6-311+G(d,p)	-5041.837824		-5041.893121	-5041.806676
	MP2/6-311G(2df,p)	-5041.861600		-5041.914787	-5041.807535
	MP4/6-311G(2df,p)	-5041.914106		-5041.965061	-5041.871740
	MP2/6-311+G(3df,2p)	-5041.881512		-5041.934933	-5041.827812
GaO_2	MP2/6-311G(d,p)	-2073.262473	-2072.991256		-2073.092897
	MP4/6-311G(d,p)	-2073.291798	-2073.021666		-2073.146564
	QCISD(T)/6-311G(d,p)	-2073.284707	-2073.030699		-2073.184013
	MP2/6-311+G(d,p)	-2073.272060	-2072.999630		-2073.100871
	MP4/6-311+G(d,p)	-2073.300892	-2073.030585		-2073.155280
	MP2/6-311G(2df,p)	-2073.343119	-2073.066791		-2073.158110
	MP4/6-311G(2df,p)	-2073.372882	-2073.100201		-2073.215378
	MP2/6-311+G(3df,2p)	-2073.358439	-2073.082862		-2073.173699
GaS_2	MP2/6-311G(d,p)	-2718.595283		-2718.592504	-2718.479100
	MP4/6-311G(d,p)	-2718.638150		-2718.635637	-2718.536926
	QCISD(T)/6-311G(d,p)	-2718.643387		-2718.641216	-2718.550209
	MP2/6-311+G(d,p)	-2718.597906		-2718.595221	-2718.482246
	MP4/6-311+G(d,p)	-2718.641089		-2718.638677	-2718.540480
	MP2/6-311G(2df,p)	-2718.686258		-2718.682730	-2718.561391
	MP4/6-311G(2df,p)	-2718.741855		-2718.738538	-2718.633628
	MP2/6-311+G(3df,2p)	-2718.698555		-2718.694980	-2718.573849
$GaSe_2$	MP2/6-311G(d,p)	-6723.139737	-6722.996143	-6723.135656	-6723.040011
	MP4/6-311G(d,p)	-6723.179168	-6723.045333	-6723.175403	-6723.091033
	QCISD(T)/6-311G(d,p)	-6723.183616	-6723.043812	-6723.180234	-6723.102667
	MP2/6-311+G(d,p)	-6723.140776	-6722.997963	-6723.136695	-6723.041595
	MP4/6-311+G(d,p)	-6723.180294	-6723.047235	-6723.176559	-6723.092765
	MP2/6-311G(2df,p)	-6723.198472	-6723.051220	-6723.194197	-6723.090699
	MP4/6-311G(2df,p)	-6723.247889	-6723.110988	-6723.243883	-6723.152669
	MP2/6-311+G(3df,2p)	-6723.221259	-6723.075074	-6723.216997	-6723.114183
ClO_2	MP2/6-311G(d,p)	-609.558448	-609.474857	-609.550259	-609.486767
	MP4/6-311G(d,p)	-609.688113	-609.524871	-609.585718	-609.534197
	QCISD(T)/6-311G(d,p)	-609.498876	-609.509811	-609.577506	-609.539790
	MP2/6-311+G(d,p)	-609.556193	-609.488652	-609.568403	-609.499397
	MP4/6-311+G(d,p)	-609.671157	-609.540640	-609.605460	-609.547872
	MP2/6-311G(2df,p)	-609.674976	-609.616671	-609.716495	-609.609334
	MP4/6-311G(2df,p)	-609.779479	-609.679058	-609.762827	-609.671086
	MP2/6-311+G(3df,2p)	-609.676571	-609.642137	-609.750843	-609.631495

Table 4. (cont'd.)

Species	Calculational Level	linear E(T) doublet	linear E(T) quartet	nonlinear E(T) doublet	nonlinear E(T) quartet
ClS_2	MP2/6-311G(d,p)			-1254.804219	
	MP4/6-311G(d,p)			-1254.857621	
	QCISD(T)/6-311G(d,p)			-1254.861512	
	MP2/6-311+G(d,p)			-1254.813103	
	MP4/6-311+G(d,p)			-1254.867091	
	MP2/6-311G(2df,p)			-1254.971800	
	MP4/6-311G(2df,p)			-1255.044036	
	MP2/6-311+G(3df,2p)			-1254.987212	
$ClSe_2$	MP2/6-311G(d,p)	-5259.334753		-5259.367648	
	MP4/6-311G(d,p)	-5259.390835		-5259.417325	
	QCISD(T)/6-311G(d,p)	-5259.411454		-5259.421985	
	MP2/6-311+G(d,p)	-5259.340564		-5259.373060	
	MP4/6-311+G(d,p)	-5259.397097		-5259.423184	
	MP2/6-311G(2df,p)	-5259.442325		-5259.487569	
	MP4/6-311G(2df,p)	-5259.513510		-5259.553236	
	MP2/6-311+G(3df,2p)	-5259.468034		-5259.512949	
BrO_2	MP2/6-311G(d,p)		-2722.348986	-2722.419946	-2722.342635
	MP4/6-311G(d,p)		-2722.398660	-2722.455402	-2722.391816
	QCISD(T)/6-311G(d,p)		-2722.386151	-2722.445410	-2722.380934
	MP2/6-311+G(d,p)		-2722.362448	-2722.436996	-2722.356191
	MP4/6-311+G(d,p)		-2722.413828	-2722.474091	-2722.407096
	MP2/6-311G(2df,p)		-2722.469838	-2722.559284	-2722.464213
	MP4/6-311G(2df,p)		-2722.529723	-2722.603637	-2722.523734
	MP2/6-311+G(3df,2p)		-2722.500263	-2722.593217	-2722.494872
BrS_2	MP2/6-311G(d,p)			-3367.684379	
	MP4/6-311G(d,p)			-3367.734772	
	QCISD(T)/6-311G(d,p)			-3367.738001	
	MP2/6-311+G(d,p)			-3367.690543	
	MP4/6-311+G(d,p)			-3367.741490	
	MP2/6-311G(2df,p)			-3367.825364	
	MP4/6-311G(2df,p)			-3367.893636	
	MP2/6-311+G(3df,2p)			-3367.846201	
$BrSe_2$	MP2/6-311G(d,p)		-7372.243549	-7372.244729	-7372.239118
	MP4/6-311G(d,p)		-7372.289992	-7372.290899	-7372.285998
	QCISD(T)/6-311G(d,p)		-7372.282767	-7372.295028	-7372.279791
	MP2/6-311+G(d,p)		-7372.245895	-7372.247757	-7372.241503
	MP4/6-311+G(d,p)		-7372.292840	-7372.294279	-7372.288916
	MP2/6-311G(2df,p)		-7372.327580	-7372.338631	-7372.322882
	MP4/6-311G(2df,p)		-7372.390975	-7372.400304	-7372.386606
	MP2/6-311+G(3df,2p)		-7372.358300	-7372.371908	-7372.353907

[a] Energies in hartree (au).

[b] If there is no entry, a stable geometrical arrangement was not found.

Table 5. Energies for Diatomic Neutral Molecules[a]

Species	Calculational Level	E(T) doublet	E(T) quartet
BO	MP2/6-311G(d,p)	-99.801249	-99.475926
	MP4/6-311G(d,p)	-99.816906	-99.496194
	QCISD(T)/6-311G(d,p)	-99.816969	-99.499604
	MP2/6-311+G(d,p)	-99.805332	-99.481222
	MP4/6-311+G(d,p)	-99.820935	-99.501622
	MP2/6-311G(2df,p)	-99.848000	-99.522009
	MP4/6-311G(2df,p)	-99.865584	-99.545150
	MP2/6-311+G(3df,2p)	-99.856581	-99.530649
BS	MP2/6-311G(d,p)	-422.358072	-422.096738
	MP4/6-311G(d,p)	-422.385634	-422.125016
	QCISD(T)/6-311G(d,p)	-422.389811	-422.131062
	MP2/6-311+G(d,p)	-422.359994	-422.098648
	MP4/6-311+G(d,p)	-422.387783	-422.127124
	MP2/6-311G(2df,p)	-422.405933	-422.144896
	MP4/6-311G(2df,p)	-422.439314	-422.180940
	MP2/6-311+G(3df,2p)	-422.411455	-422.150205
BSe	MP2/6-311G(d,p)	-2424.606292	-2424.474056
	MP4/6-311G(d,p)	-2424.633569	-2424.501175
	QCISD(T)/6-311G(d,p)	-2424.638302	-2424.505574
	MP2/6-311+G(d,p)	-2424.607041	-2424.475052
	MP4/6-311+G(d,p)	-2424.634404	-2424.502265
	MP2/6-311G(2df,p)	-2424.639791	-2424.504717
	MP4/6-311G(2df,p)	-2424.671422	-2424.536554
	MP2/6-311+G(3df,2p)	-2424.649358	-2424.514858
AlO	MP2/6-311G(d,p)	-316.972901	-316.809400
	MP4/6-311G(d,p)	-317.000367	-316.825792
	QCISD(T)/6-311G(d,p)	-317.018321	-316.828230
	MP2/6-311+G(d,p)	-316.983053	-316.819299
	MP4/6-311+G(d,p)	-317.010772	-316.836017
	MP2/6-311G(2df,p)	-317.025877	-316.862752
	MP4/6-311G(2df,p)	-317.055912	-316.883030
	MP2/6-311+G(3df,2p)	-317.035671	-316.871972
AlS	MP2/6-311G(d,p)	-639.623860	-639.429744
	MP4/6-311G(d,p)	-639.649945	-639.452928
	QCISD(T)/6-311G(d,p)	-639.652856	-639.456966
	MP2/6-311+G(d,p)	-639.625415	-639.431438
	MP4/6-311+G(d,p)	-639.651762	-639.454819
	MP2/6-311G(2df,p)	-639.680112	-639.485812
	MP4/6-311G(2df,p)	-639.711916	-639.518067
	MP2/6-311+G(3df,2p)	-639.684412	-639.489416

Table 5. (cont'd.)

Species	Calculational Level	E(T) doublet	E(T) quartet
AlSe	MP2/6-311G(d,p)	-2641.893347	-2641.787291
	MP4/6-311G(d,p)	-2641.917656	-2641.810658
	QCISD(T)/6-311G(d,p)	-2641.920330	-2641.814136
	MP2/6-311+G(d,p)	-2641.894271	-2641.788350
	MP4/6-311+G(d,p)	-2641.918634	-2641.811800
	MP2/6-311G(2df,p)	-2641.928749	-2641.819408
	MP4/6-311G(2df,p)	-2641.958645	-2641.848943
	MP2/6-311+G(3df,2p)	-2641.938976	-2641.829760
GaO	MP2/6-311G(d,p)	-1998.229007	-1998.117866
	MP4/6-311G(d,p)	-1998.253167	-1998.135460
	QCISD(T)/6-311G(d,p)	-1998.265917	-1998.138919
	MP2/6-311+G(d,p)	-1998.234357	-1998.122935
	MP4/6-311+G(d,p)	-1998.258555	-1998.140634
	MP2/6-311G(2df,p)	-1998.267797	-1998.154266
	MP4/6-311G(2df,p)	-1998.291910	-1998.173069
	MP2/6-311+G(3df,2p)	-1998.279187	-1998.165550
GaS	MP2/6-311G(d,p)	-2320.914941	-2320.800638
	MP4/6-311G(d,p)	-2320.941729	-2320.827079
	QCISD(T)/6-311G(d,p)	-2320.944499	-2320.831139
	MP2/6-311+G(d,p)	-2320.916166	-2320.802486
	MP4/6-311+G(d,p)	-2320.943187	-2320.829073
	MP2/6-311G(2df,p)	-2320.962767	-2320.843882
	MP4/6-311G(2df,p)	-2320.994865	-2320.877399
	MP2/6-311+G(3df,2p)	-2320.972232	-2320.853360
GaSe	MP2/6-311G(d,p)	-4323.185109	-4323.087384
	MP4/6-311G(d,p)	-4323.210188	-4323.112491
	QCISD(T)/6-311G(d,p)	-4323.212805	-4323.116245
	MP2/6-311+G(d,p)	-4323.185769	-4323.088241
	MP4/6-311+G(d,p)	-4323.210888	-4323.113383
	MP2/6-311G(2df,p)	-4323.215949	-4323.113656
	MP4/6-311G(2df,p)	-4323.245880	-4323.143462
	MP2/6-311+G(3df,2p)	-4323.230860	-4323.128987
ClO	MP2/6-311G(d,p)	-534.568520	-534.506015
	MP4/6-311G(d,p)	-534.600753	-534.538921
	QCISD(T)/6-311G(d,p)	-534.605645	-534.540867
	MP2/6-311+G(d,p)	-534.577210	-534.510180
	MP4/6-311+G(d,p)	-534.610191	-534.543543
	MP2/6-311G(2df,p)	-534.662573	-534.578933
	MP4/6-311G(2df,p)	-534.706068	-534.624566
	MP2/6-311+G(3df,2p)	-534.678539	-534.588865

Table 5. (cont'd.)

Species	Calculational Level	E(T) doublet	E(T) quartet
ClS	MP2/6-311G(d,p)	-857.241878	-857.183400
	MP4/6-311G(d,p)	-857.276218	-857.218748
	QCISD(T)/6-311G(d,p)	-857.278641	-857.226908
	MP2/6-311+G(d,p)	-857.246834	-857.187570
	MP4/6-311+G(d,p)	-857.281514	-857.223281
	MP2/6-311G(2df,p)	-857.343974	-857.272570
	MP4/6-311G(2df,p)	-857.393041	-857.322749
	MP2/6-311+G(3df,2p)	-857.352750	-857.281489
ClSe	MP2/6-311G(d,p)	-2859.525833	-2859.476728
	MP4/6-311G(d,p)	-2859.558286	-2859.509426
	QCISD(T)/6-311G(d,p)	-2859.560503	-2859.515405
	MP2/6-311+G(d,p)	-2859.529095	-2859.479404
	MP4/6-311+G(d,p)	-2859.561843	-2859.512460
	MP2/6-311G(2df,p)	-2859.607457	-2859.549874
	MP4/6-311G(2df,p)	-2859.652051	-2859.593951
	MP2/6-311+G(3df,2p)	-2859.621837	-2859.564186
BrO	MP2/6-311G(d,p)	-2647.428903	-2647.373519
	MP4/6-311G(d,p)	-2647.459687	-2647.404181
	QCISD(T)/6-311G(d,p)	-2647.465799	-2647.405858
	MP2/6-311+G(d,p)	-2647.435826	-2647.376938
	MP4/6-311+G(d,p)	-2647.467372	-2647.407973
	MP2/6-311G(2df,p)	-2647.504935	-2647.430277
	MP4/6-311G(2df,p)	-2647.545193	-2647.471192
	MP2/6-311+G(3df,2p)	-2647.525651	-2647.447292
BrS	MP2/6-311G(d,p)	-2970.103258	-2970.047721
	MP4/6-311G(d,p)	-2970.135794	-2970.081139
	QCISD(T)/6-311G(d,p)	-2970.138414	-2970.090289
	MP2/6-311+G(d,p)	-2970.106535	-2970.050944
	MP4/6-311+G(d,p)	-2970.139290	-2970.084551
	MP2/6-311G(2df,p)	-2970.182511	-2970.116463
	MP4/6-311G(2df,p)	-2970.228606	-2970.163543
	MP2/6-311+G(3df,2p)	-2970.198855	-2970.132471
BrSe	MP2/6-311G(d,p)	-4972.386902	-4972.338773
	MP4/6-311G(d,p)	-4972.417352	-4972.369597
	QCISD(T)/6-311G(d,p)	-4972.419708	-4972.376609
	MP2/6-311+G(d,p)	-4972.388416	-4972.340603
	MP4/6-311+G(d,p)	-4972.419000	-4972.371571
	MP2/6-311G(2df,p)	-4972.445901	-4972.391642
	MP4/6-311G(2df,p)	-4972.487467	-4972.432942
	MP2/6-311+G(3df,2p)	-4972.468223	-4972.413142

[a] Energies in hartree (au).

Table 6. Correction Terms and G2/G2(MP2) Energies for Triatomic Molecules[a,b]

Species	Calculational Level	linear		nonlinear	
		E(T) doublet	E(T) quartet	E(T) doublet	E(T) quartet
BO_2	ZPE	0.009113	0.012358	0.009194	0.006233
	Enthalpy correction	0.012984	0.016203	0.013278	0.010398
	HLC	-0.035190	-0.030570	-0.035190	-0.030570
	G2	-175.070677	-174.770825	-175.064428	-174.905089
	G2(MP2)	-175.065940	-174.764267	-175.059622	-174.899171
BS_2	ZPE	0.005201		0.002343	
	Enthalpy correction	0.009607		0.007431	
	HLC	-0.035190		-0.035190	
	G2	-820.290840		-820.288763	
	G2(MP2)	-820.277378		-820.275125	
BSe_2	ZPE	0.013277		0.003391	
	Enthalpy correction	0.017939		0.008081	
	HLC	-0.035190		-0.035190	
	G2	-4824.668498		-4824.763859	
	G2(MP2)	-4824.659461		-4824.754580	
AlO_2	ZPE			0.005019	0.003679
	Enthalpy correction			0.009515	0.008314
	HLC			-0.035190	-0.030570
	G2			-392.231697	-392.034932
	G2(MP2)			-392.225298	-392.027463
AlS_2	ZPE	0.003726		0.002036	
	Enthalpy correction	0.008660		0.007150	
	HLC	-0.035190		-0.035190	
	G2	-1037.462527		-1037.512378	
	G2(MP2)	-1037.448452		-1037.498572	
$AlSe_2$	ZPE	0.002305		0.002189	0.003699
	Enthalpy correction	0.007700		0.007344	0.008690
	HLC	-0.035190		-0.035190	-0.030570
	G2	-5041.971461		-5042.022829	-5041.931453
	G2(MP2)	-5041.960328		-5042.012036	-5041.919528

Table 6. (cont'd.)

Species	Calculational Level	linear E(T) doublet	linear E(T) quartet	nonlinear E(T) doublet	nonlinear E(T) quartet
GaO_2	ZPE	0.004633	0.003931		0.002439
	Enthalpy correction	0.009326	0.008606		0.007485
	HLC	-0.035190	-0.030570		-0.030570
	G2	-2073.411174	-2073.152489		-2073.297290
	G2(MP2)	-2073.411230	-2073.148944		-2073.292946
GaS_2	ZPE	0.002583		0.002394	0.004405
	Enthalpy correction	0.007900		0.007418	0.009259
	HLC	-0.035190		-0.035190	-0.030570
	G2	-2718.792312		-2718.789487	-2718.685941
	G2(MP2)	-2718.779266		-2718.776488	-2718.671123
$GaSe_2$	ZPE	0.001844	0.008686	0.001682	0.003107
	Enthalpy correction	0.007514	0.013615	0.007035	0.008183
	HLC	-0.035190	-0.030570	-0.035190	-0.030570
	G2	-6723.308555	-6723.155287	-6723.305140	-6723.215398
	G2(MP2)	-6723.298484	-6723.144627	-6723.295083	-6723.204301
ClO_2	ZPE	0.015789	0.009187	0.005357	0.001877
	Enthalpy correction	0.019286	0.013511	0.009517	0.007566
	HLC	-0.045190	-0.045700	-0.045190	-0.040570
	G2	-609.606536	-609.727949	-609.830394	-609.738579
	G2(MP2)	-609.646400	-609.713603	-609.817922	-609.723211
ClS_2	ZPE			0.002582	
	Enthalpy correction			0.007418	
	HLC			-0.045190	
	G2			-1255.106534	
	G2(MP2)			-1255.087113	
$ClSe_2$	ZPE	0.001885		0.001954	
	Enthalpy correction	0.007521		0.007114	
	HLC	-0.045190		-0.045190	
	G2	-5259.603594		-5259.626958	
	G2(MP2)	-5259.588041		-5259.610521	

Table 6. (cont'd.)

Species	Calculational Level	linear E(T) doublet	linear E(T) quartet	nonlinear E(T) doublet	nonlinear E(T) quartet
BrO_2	ZPE		0.010467	0.004492	0.030213
	Enthalpy correction		0.014919	0.008819	0.034650
	HLC		-0.040570	-0.045190	-0.040570
	G2		-2722.579449	-2722.669917	-2722.555593
	G2(MP2)		-2722.567530	-2722.659380	-2722.543527
BrS_2	ZPE			0.002205	
	Enthalpy correction			0.007215	
	HLC			-0.045190	
	G2			-3367.961241	
	G2(MP2)			-3367.942808	
$BrSe_2$	ZPE		0.001940	0.001533	0.001811
	Enthalpy correction		0.007631	0.006919	0.007165
	HLC		-0.040570	-0.045190	-0.040570
	G2		-7372.453602	-7372.481718	-7372.450715
	G2(MP2)		-7372.436148	-7372.465864	-7372.433339

[a] Energies in hartree (au).
[b] If there is no entry, a stable geometrical arrangement was not found.

Table 7. Correction Terms and G2/G2(MP2) Energies for Diatomic molecules[a]

Species	Calculational Level	E(T) doublet	E(T) quartet
BO	ZPE	0.004253	0.002702
	Enthalpy correction	0.007559	0.006024
	HLC	-0.020190	-0.015570
	G2	-99.890111	-99.570199
	G2(MP2)	-99.888238	-99.567195
BS	ZPE	0.002694	0.001799
	Enthalpy correction	0.006017	0.005185
	HLC	-0.020190	-0.015570
	G2	-422.466736	-422.206265
	G2(MP2)	-422.460691	-422.198300
BSe	ZPE	0.002204	0.001431
	Enthalpy correction	0.005550	0.004880
	HLC	-0.020190	-0.015570
	G2	-2424.703793	-2424.565327
	G2(MP2)	-2424.699355	-2424.560515
AlO	ZPE	0.001727	0.001753
	Enthalpy correction	0.005123	0.005145
	HLC	-0.020190	-0.015570
	G2	-317.102377	-316.908830
	G2(MP2)	-317.099554	-316.904619
AlS	ZPE	0.001538	0.001020
	Enthalpy correction	0.004966	0.004590
	HLC	-0.020190	-0.015570
	G2	-639.738042	-639.540455
	G2(MP2)	-639.732060	-639.531188
AlSe	ZPE	0.001193	0.000741
	Enthalpy correction	0.004705	0.004435
	HLC	-0.020190	-0.015570
	G2	-2641.990597	-2641.877684
	G2(MP2)	-2641.984956	-2641.871434
GaO	ZPE	0.001363	0.001326
	Enthalpy correction	0.004829	0.004801
	HLC	-0.020190	-0.015570
	G2	-1998.334915	-1998.202160
	G2(MP2)	-1998.334923	-1998.200847

Table 7. (cont'd.)

Species	Calculational Level	E(T) doublet	E(T) quartet
GaS	ZPE	0.001208	0.000631
	Enthalpy correction	0.004715	0.004385
	HLC	-0.020190	-0.015570
	G2	-2321.026315	-2320.906023
	G2(MP2)	-2321.020772	-2320.898800
GaSe	ZPE	0.000827	0.000485
	Enthalpy correction	0.004479	0.004330
	HLC	-0.020190	-0.015570
	G2	-4323.282811	-4323.177667
	G2(MP2)	-4323.277919	-4323.172933
ClO	ZPE	0.001817	0.000204
	Enthalpy correction	0.005201	0.004263
	HLC	-0.030190	-0.025570
	G2	-534.756048	-534.662267
	G2(MP2)	-534.744037	-534.649084
ClS	ZPE	0.001209	0.000639
	Enthalpy correction	0.004716	0.004389
	HLC	-0.030190	-0.025570
	G2	-857.433561	-857.365122
	G2(MP2)	-857.418493	-857.349928
ClSe	ZPE	0.000968	0.000601
	Enthalpy correction	0.004559	0.004373
	HLC	-0.030190	-0.025570
	G2	-2859.698164	-2859.639568
	G2(MP2)	-2859.685730	-2859.627831
BrO	ZPE	0.001680	0.000177
	Enthalpy correction	0.005083	0.004260
	HLC	-0.030190	-0.025570
	G2	-2647.601293	-2647.515650
	G2(MP2)	-2647.591056	-2647.505025
BrS	ZPE	0.000985	0.000488
	Enthalpy correction	0.004569	0.004331
	HLC	-0.030190	-0.025570
	G2	-2970.276994	-2970.213973
	G2(MP2)	-2970.263216	-2970.200121

Table 7. (cont'd.)

Species	Calculational Level	E(T) doublet	E(T) quartet
BrSe	ZPE	0.000725	0.000432
	Enthalpy correction	0.004427	0.004314
	HLC	-0.030190	-0.025570
	G2	-4972.541743	-4972.486736
	G2(MP2)	-4972.530494	-4972.476116

[a] Energies in hartree (au).

Table 8. Bond Dissociation Enthalpies for Triatomic Molecules[a,b]

Species	D°_m(G2(MP2))	D°_m(G2)	D°_m(exp)[c]
BO_2	1337	1333	1342
BS_2	1007	1002	
BSe_2	829	833	
AlO_2	894	891	914
AlS_2	726	718	
$AlSe_2$	644	648	
GaO_2	572	557	
GaS_2	653	648	
$GaSe_2$	585	592	
ClO_2	517	506	515
ClS_2	338	321	
$ClSe_2$	281	277	
BrO_2	476	467	
BrS_2	335	323	
$BrSe_2$	277	278	

[a] Enthalpies in kJ/mol.
[b] Only the most stable structures are included.
[c] Reference 72.

Table 9. Bond Dissociation Enthalpies for Diatomic Molecules[a,b]

Species	D°_{m}(G2(MP2))	D°_{m}(G2)	D°_{m}(exp)[c]
BO	809	807	
BS	558	554	594
BSe	469	472	
AlO	505	501	512
AlS	411	403	368
AlSe	360	361	
GaO	312	306	
GaS	358	355	
GaSe	318	323	
ClO	262	259	269
ClS	278	271	242
ClSe	265	260	
BrO	237	236	
BrS	247	243	
BrSe	233	233	

[a] Enthalpies in kJ/mol.
[b] Only the most stable structures are included.
[c] Reference 72.

Table 10. Ratio of Bond Dissociation Enthalpies, $D^{\circ}_{m}(AB_2)/2D^{\circ}_{m}(AB)$

Species	G2(MP2) ratio	G2 ratio	Exp. ratio
BO_2/BO	0.83	0.83	
BS_2/BS	0.90	0.90	
BSe_2/BSe	0.88	0.88	
AlO_2/AlO	0.89	0.89	
AlS_2/AlS	0.88	0.89	
$AlSe_2$/AlSe	0.90	0.90	
GaO_2/GaO	0.91	0.91	
GaS_2/GaS	0.91	0.91	
$GaSe_2$/GaSe	0.92	0.92	
ClO_2/ClO	0.98	0.98	0.96
ClS_2/ClS	0.61	0.59	
$ClSe_2$/ClSe	0.53	0.53	
BrO_2/BrO	1.00	0.99	
BrS_2/BrS	0.68	0.66	
$BrSe_2$/BrSe	0.59	0.60	

Table 11. Backbone Dihedral Angles[a] of ATCh and Complexes

Molecule[b]	$\angle C_4N_1C_5C_6$	$\angle N_1C_5C_6S_7$	$\angle C_5C_6S_7C_8$	$\angle C_6S_7C_8C_{10}$
ATCh, gg'	172.0	83.2	-108.3	-167.2
ATCh(H_2O), gg', br	-171.9	97.9	-122.1	-171.4
ATCh(H_2O), gg', qa	172.6	83.1	-109.1	-167.7
ATCh(H_2O), gg', qa3m	172.3	83.7	-109.1	-167.8
ATCh(C_6H_6), gg', qa	171.5	82.9	-108.7	-167.3
ATCh(C_6H_6), gg', qa3m	172.2	83.5	-109.0	-167.7
ATCh(C_6H_6)(H_2O), gg', qa, qa3m	171.9	83.4	-109.5	-167.9
ATCh(C_6H_6)(H_2O), gg', qa3m, qa	172.7	84.0	-109.9	-168.0
ATCh, gg	-175.7	89.1	72.6	172.1
ATCh(H_2O), gg, br	169.7	70.1	67.3	171.3
ATCh(H_2O), gg, qa	-177.0	89.4	73.5	172.2
ATCh(H_2O), gg, qa3m	-175.7	89.5	73.0	172.4
ATCh(C_6H_6), gg, qa	-176.2	89.5	73.0	172.6
ATCh(C_6H_6), gg, qa3m	-175.7	89.7	72.9	172.3
ATCh(C_6H_6)(H_2O), gg, qa, br	167.5	68.3	67.6	171.8
ATCh(C_6H_6)(H_2O), gg, qa, qa3m	-176.6	90.3	73.4	173.0
ATCh(C_6H_6)(H_2O), gg, qa3m, br	-175.2	92.5	75.6	173.6
ATCh(C_6H_6)(H_2O), gg, qa3m, qa	-175.2	90.6	73.2	172.9
ATCh(H_2O), gt, br	-172.6	99.0	-151.0	-172.1
ATCh(H_2O), gt, qa	-177.4	87.4	168.5	-177.6
ATCh(C_6H_6)(H_2O), gt, qa, qa3m	171.2	78.4	170.8	-178.1

Table 11. (cont'd.)

Molecule	$\angle C_4N_1C_5C_6$	$\angle N_1C_5C_6S_7$	$\angle C_5C_6S_7C_8$	$\angle C_6S_7C_8C_{10}$
ATCh, tg	-178.0	-168.0	76.9	174.2
ATCh(H_2O), tg, br	-169.3	-171.0	80.5	175.9
ATCh(H_2O), tg, qa	-178.5	-169.8	77.3	174.6
ATCh(H_2O), tg, qa3m	-178.1	-169.3	77.3	174.5
ATCh(C_6H_6), tg, qa	-173.5	-166.2	77.3	174.3
ATCh(C_6H_6), tg, qa3m	-177.9	-169.3	77.2	174.4
ATCh(C_6H_6)(H_2O), tg, qa, qa3m	-174.0	-167.6	77.8	174.6
ATCh(C_6H_6)(H_2O), tg, qa3m, qa	-177.4	-170.0	77.7	174.6
ATCh, tt	-180.0	-180.0	-180.0	180.0
ATCh(H_2O), tt, br	-179.9	-179.8	-180.0	178.8
ATCh(H_2O), tt, qa	-179.5	179.9	178.7	-179.3
ATCh(H_2O), tt, qa3m	-180.0	180.0	-180.0	-180.0
ATCh(C_6H_6), tt, qa	-178.9	-178.5	173.9	-180.0
ATCh(C_6H_6), tt, qa3m	180.0	180.0	180.0	180.0
ATCh(C_6H_6)(H_2O), tt, qa3m, qa	179.1	-179.9	-178.3	179.0

[a]Dihedral angles in degrees. See **Scheme 1** for ATCh numbering scheme.
[b]ATCh: acetylthiocholine, g: gauche, g': gauche', t: trans. See text for abbreviations.

Table 12. Hydrogen Bond Lengths and Angles[a,b]

Molecule	$S_7 \cdots H_{13}$	Angle[c]	$O_9 \cdots H$	Angle[c]	$O_{27} \cdots H$	Angle[c]
ATCh,	2.958	113.8	2.414(13)	151.2		
gg'			2.467(15)	148.9		
			2.390(23)	106.6		
ATCh(H_2O),	3.164	101.3	2.464(13)	154.3	2.194(15)	171.9
gg', br			2.375(23)	111.8	2.492(23)	171.1
			2.157(28)	136.9		
ATCh(H_2O),	2.956	113.2	2.425(13)	151.9	2.791(12)	142.3
gg', qa			2.513(15)	148.4	2.495(16)	151.6
			2.386(23)	107.3	2.468(20)	157.5
ATCh(H_2O),	2.963	113.5	2.437(13)	152.1	2.534(12)	149.3
gg', qa3m			2.522(15)	148.6	2.514(16)	150.0
			2.384(23)	107.4	2.596(18)	147.7
ATCh(C_6H_6),	2.943	114.8	2.457(13)	150.3		
gg', qa			2.455(15)	149.9		
			2.389(23)	106.9		
ATCh(C_6H_6),	2.959	113.8	2.435(13)	151.8		
gg', qa3m			2.508(15)	148.8		
			2.385(23)	107.2		
ATCh(C_6H_6)(H_2O),	2.948	114.4	2.479(13)	151.0	2.571(12)	148.9
gg', qa, qa3m			2.505(15)	149.7	2.504(16)	151.2
			2.382(23)	107.8	2.629(18)	147.5
ATCh(C_6H_6)(H_2O),	2.947	114.4	2.462(13)	152.1	2.556(12)	149.5
gg', qa3m, qa			2.544(15)	148.7	2.768(16)	142.6
			2.376(23)	108.0	2.417(20)	156.6
ATCh,	2.962	107.2	2.537(20)	109.3		
gg			2.517(22)	93.4		
ATCh(H_2O),	2.769	121.6	2.458(20)	117.9	2.468(12)	149.1
gg, br			2.271(28)	134.9	2.688(16)	141.9
					2.347(20)	156.2
ATCh(H_2O),	2.983	105.9	2.573(20)	108.6	2.500(12)	155.1
gg, qa			2.515(22)	94.2	2.558(16)	151.1
					2.534(23)	140.1
ATCh(H_2O),	2.970	107.2	2.557(20)	108.9	2.698(12)	144.8
gg, qa3m			2.515(22)	93.8	2.453(16)	153.2
					2.521(18)	150.3
ATCh(C_6H_6),	2.963	107.6	2.567(20)	108.6		
gg, qa			2.514(22)	93.9		
ATCh(C_6H_6),	2.968	107.4	2.554(20)	108.8		
gg, qa3m			2.517(22)	93.6		
ATCh(C_6H_6)(H_2O),	2.763	122.9	2.438(12)	117.6	2.359(12)	157.0
gg, qa, br			2.257(28)	136.4	2.450(16)	150.5
					2.774(18)	140.2

Table 12. (cont'd.)

Molecule	$S_7 \cdots H_{13}$	Angle[c]	$O_9 \cdots H$	Angle[c]	$O_{27} \cdots H$	Angle[c]
ATCh(C_6H_6)(H_2O), gg, qa, qa3m	2.974	107.8	2.590(20) 2.512(22)	107.9 94.2	2.515(12) 2.525(16) 2.675(18)	151.0 150.8 146.0
ATCh(C_6H_6)(H_2O), gg, qa3m, br	3.019	106.5	2.716(20) 2.525(22) 2.230(28)	105.3 95.4 140.4	2.358(21) 2.597(22)	124.2 125.4
ATCh(C_6H_6)(H_2O), gg, qa3m, qa	2.984	106.9	2.582(20) 2.516(22)	107.9 93.9	2.663(16) 2.496(18) 2.532(20)	146.0 151.8 153.0
ATCh(H_2O), gt, br	3.193(11) 3.192(13)	98.0 98.1	2.377(22) 2.082(28)	108.3 144.4	2.503(12) 2.322(16) 2.514(22)	147.4 150.6 160.9
ATCh(H_2O), gt, qa	2.865	108.3	2.537(22)	91.6	2.468(12) 2.651(18) 2.441(20)	148.8 142.9 148.5
ATCh(C_6H_6)(H_2O), gt, qa, qa3m	2.739	117.2			2.652(12) 2.455(16) 2.592(20)	146.5 153.5 148.1
ATCh, tg			2.482(20) 2.494(23)	114.2 94.4		
ATCh(H_2O), tg, br			2.640(20) 2.510(23) 2.321(28)	112.3 95.9 131.4	2.247(16) 2.368(23)	158.7 169.4
ATCh(H_2O), tg, qa			2.496(20) 2.499(23)	114.7 94.8	2.553(12) 2.496(16) 2.621(21)	148.3 150.3 148.1
ATCh(H_2O), tg, qa3m			2.497(20) 2.496(23)	114.3 94.7	2.542(12) 2.457(16) 2.672(18)	149.0 152.5 144.3
ATCh(C_6H_6), tg, qa			2.515(20) 2.499(23)	112.9 94.4		
ATCh(C_6H_6), tg, qa3m			2.484(20) 2.496(23)	114.3 94.7		
ATCh(C_6H_6)(H_2O), tg, qa, qa3m			2.531(20) 2.501(23)	113.2 94.7	2.653(12) 2.512(16) 2.555(20)	146.3 150.8 149.1
ATCh(C_6H_6)(H_2O), tg, qa3m, qa			2.514(20) 2.499(23)	114.4 94.9	2.561(12) 2.522(16) 2.642(18)	149.0 150.1 148.1

Table 12. (cont'd.)

Molecule	$S_7 \cdots H_{13}$	Angle[c]	$O_9 \cdots H$	Angle[c]	$O_{27} \cdots H$	Angle[c]
ATCh(H_2O),					2.524(15)	154.6
tt, br					2.526(18)	154.6
			2.237(28)	154.1	2.618(22)	105.5
					2.609(23)	106.1
ATCh(H_2O),					2.552(12)	147.6
tt, qa					2.467(18)	150.2
					2.592(20)	148.8
ATCh(H_2O),					2.633(12)	145.8
tt, qa3m					2.499(15)	149.6
					2.499(16)	149.7
ATCh(C_6H_6),			2.539(23)	90.7		
tt, qa						
ATCh(C_6H_6)(H_2O),					2.652(12)	145.5
tt, qa3m, qa					2.488(16)	151.0
					2.532(20)	151.1

[a]Only those ions with X-H····O or S hydrogen bonds are included. HF/6-31G(d) bond lengths in Å, bond angles in degrees.

[b]The numbers in parentheses indicate the hydrogen to which oxygen is hydrogen bonded. See **Scheme 1** for ATCh numbering scheme. Numbering scheme for water molecule: $H_{28}O_{27}H_{29}$.

[c]Angle X-H····O, where X = C or H.

Table 13. Total Energies

Molecule	HF/6-31G(d)[a]	MP2/6-31G(d)[a]	MP2/6-31+G(d)[a]	ZPE[a,b]
ATCh,gg'	-800.999541	-802.378483	-802.398678	0.249494
ATCh,gg	-800.997787	-802.374889	-802.395234	0.249023
ATCh,tg	-801.003380	-802.380127	-802.400700	0.249240
ATCh,tt	-800.996649	-802.371940	-802.392167	0.248788
ATCh(H_2O),gg', br	-877.025496	-878.593588	-878.625679	0.275188
ATCh(H_2O),gg', qa	-877.026512	-878.594328	-878.625968	0.274817
ATCh(H_2O),gg', qa3m	-877.026423	-878.594180	-878.625596	0.274890
ATCh(H_2O),gg, br	-877.026991	-878.594505	-878.626957	0.275386
ATCh(H_2O),gg, qa	-877.025187	-878.591738	-878.623475	0.274580
ATCh(H_2O),gg, qa3m	-877.025140	-878.591194	-878.622585	0.274430
ATCh(H_2O),gt, br	-877.025189	-878.592367	-878.624961	0.275359
ATCh(H_2O),gt, qa	-877.021690	-878.587655	-878.619545	0.274392
ATCh(H_2O),tg, br	-877.029788	-878.596274	-878.629070	0.275155
ATCh(H_2O),tg, qa	-877.030519	-878.596136	-878.628267	0.274641
ATCh(H_2O),tg, qa3m	-877.030607	-878.596156	-878.627846	0.274637
ATCh(H_2O),tt, br	-877.028320	-878.594617	-878.626054	0.275713
ATCh(H_2O),tt, qa	-877.024390	-878.588695	-878.620540	0.274290
ATCh(H_2O),tt, qa3m	-877.024409	-878.588583	-878.619922	0.274251
ATCh(C_6H_6),gg', qa	-1031.712416	-1033.850284	-1033.886419	0.358090
ATCh(C_6H_6),gg', qa3m	-1031.712498	-1033.849588	-1033.885011	0.358087
ATCh(C_6H_6),gg, qa	-1031.711279	-1033.847103	-1033.883686	0.357655
ATCh(C_6H_6),gg, qa3m	-1031.711158	-1033.846425	-1033.881831	0.357662
ATCh(C_6H_6),tg, qa	-1031.716789	-1033.852714	-1033.889697	0.357899
ATCh(C_6H_6),tg, qa3m	-1031.716646	-1033.851483	-1033.886996	0.357855
ATCh(C_6H_6),tt, qa	-1031.710332	-1033.844771	-1033.881146	0.357454
ATCh(C_6H_6),tt, qa3m	-1031.710325	-1033.843822	-1033.879003	0.357440
ATCh(C_6H_6)(H_2O),gg', qa, qa3m	-1107.738285	-1110.064709	-1110.112337	0.383375
ATCh(C_6H_6)(H_2O),gg', qa3m, qa	-1107.738374	-1110.064243	-1110.111491	0.383397
ATCh(C_6H_6)(H_2O),gg, qa, br	-1107.739604	-1110.065881	-1110.115190	0.383980
ATCh(C_6H_6)(H_2O),gg, qa, qa3m	-1107.737554	-1110.062025	-1110.110256	0.382933
ATCh(C_6H_6)(H_2O),gg, qa3m, br	-1107.737054	-1110.061049	-1110.109424	0.383436
ATCh(C_6H_6)(H_2O),gg, qa3m, qa	-1107.737514	-1110.061353	-1110.108583	0.382989
ATCh(C_6H_6)(H_2O),gt, qa, qa3m	-1107.733626	-1110.057899	-1110.105595	0.382807
ATCh(C_6H_6)(H_2O),tg, qa, qa3m	-1107.742919	-1110.067377	-1110.115742	0.383159
ATCh(C_6H_6)(H_2O),tg, qa3m, qa	-1107.742704	-1110.066028	-1110.113395	0.383137
ATCh(C_6H_6)(H_2O),tt, qa3m, qa	-1107.736968	-1110.059070	-1110.106163	0.382796
C_6H_6	-230.703137	-231.456505	-231.470391	0.107673
H_2O	-76.010747	-76.195958	-76.208700	0.022977

[a]Energies in hartrees (au).
[b]ZPE: Zero Point Energy.

Table 14. HF/6-31G(d) Entropies and Thermochemical Corrections

Molecule	Energy correction[a]	Enthalpy correction[a]	Gibbs free energy correction[a]	Entropy[b]
ATCh,gg'	0.261406	0.262350	0.211590	106.834000
ATCh,gg	0.261163	0.262107	0.209997	109.676000
ATCh,tg	0.261429	0.262373	0.210018	110.191000
ATCh,tt	0.261320	0.262265	0.207617	115.016000
ATCh(H_2O),gg', br	0.290671	0.291616	0.231874	125.737000
ATCh(H_2O),gg', qa	0.290724	0.291668	0.230404	128.941000
ATCh(H_2O),gg', qa3m	0.290744	0.291688	0.230624	128.519000
ATCh(H_2O),gg, br	0.290794	0.291738	0.232190	125.329000
ATCh(H_2O),gg, qa	0.290536	0.291481	0.230151	129.078000
ATCh(H_2O),gg, qa3m	0.290513	0.291457	0.228762	131.952000
ATCh(H_2O),gt, br	0.290813	0.291757	0.231523	126.772000
ATCh(H_2O),gt, qa	0.290524	0.291468	0.228287	132.977000
ATCh(H_2O),tg, br	0.290751	0.291695	0.231629	126.420000
ATCh(H_2O),tg, qa	0.290764	0.291708	0.229021	131.937000
ATCh(H_2O),tg, qa3m	0.290763	0.291707	0.228787	132.425000
ATCh(H_2O),tt, br	0.291228	0.292173	0.231536	127.621000
ATCh(H_2O),tt, qa	0.290684	0.291628	0.226972	136.081000
ATCh(H_2O),tt, qa3m	0.290681	0.291626	0.226838	136.356000
ATCh(C_6H_6),gg', qa	0.376404	0.377349	0.305631	150.942000
ATCh(C_6H_6),gg', qa3m	0.376409	0.377354	0.305256	151.743000
ATCh(C_6H_6),gg, qa	0.376189	0.377134	0.303687	154.581000
ATCh(C_6H_6),gg, qa3m	0.376190	0.377134	0.303922	154.089000
ATCh(C_6H_6),tg, qa	0.376464	0.377408	0.303753	155.020000
ATCh(C_6H_6),tg, qa3m	0.376438	0.377382	0.303880	154.699000
ATCh(C_6H_6),tt, qa	0.376364	0.377308	0.301346	159.876000
ATCh(C_6H_6),tt, qa3m	0.376350	0.377295	0.301636	159.237000
ATCh(C_6H_6)(H_2O),gg', qa, qa3m	0.405697	0.406641	0.324399	173.093000
ATCh(C_6H_6)(H_2O),gg', qa3m, qa	0.405691	0.406636	0.324232	173.433000
ATCh(C_6H_6)(H_2O),gg, qa, br	0.405812	0.406756	0.325721	170.554000
ATCh(C_6H_6)(H_2O),gg, qa, qa3m	0.405494	0.406438	0.322017	177.679000
ATCh(C_6H_6)(H_2O),gg, qa3m, br	0.405517	0.406461	0.324782	171.908000
ATCh(C_6H_6)(H_2O),gg, qa3m, qa	0.405493	0.406438	0.322794	176.043000
ATCh(C_6H_6)(H_2O),gt, qa, qa3m	0.405537	0.406481	0.320468	181.030000
ATCh(C_6H_6)(H_2O),tg, qa, qa3m	0.405747	0.406692	0.322504	177.189000
ATCh(C_6H_6)(H_2O),tg, qa3m, qa	0.405725	0.406669	0.322585	176.969000
ATCh(C_6H_6)(H_2O),tt, qa3m, qa	0.405664	0.406608	0.320487	181.258000
C_6H_6	0.111769	0.112713	0.082698	63.173000
H_2O	0.025811	0.026755	0.005380	44.987000

[a]Energies in hartrees (au).
[b]Entropis in J/(mol·K).

Table 15. HF/6-31G(d) Thermochemical Values at 298 K

Molecule	Energy[a]	Enthalpy[a]	Gibbs Free Energy[a]	Entropy[b]
ATCh,gg'	-800.738135	-800.737191	-800.787951	106.834000
ATCh,gg	-800.736624	-800.735680	-800.787790	109.676000
ATCh,tg	-800.741951	-800.741007	-800.793362	110.191000
ATCh,tt	-800.735329	-800.734384	-800.789032	115.016000
ATCh(H_2O),gg', br	-876.734825	-876.733880	-876.793622	125.737000
ATCh(H_2O),gg', qa	-876.735788	-876.734844	-876.796108	128.941000
ATCh(H_2O),gg', qa3m	-876.735679	-876.734735	-876.795799	128.519000
ATCh(H_2O),gg, br	-876.736197	-876.735253	-876.794801	125.329000
ATCh(H_2O),gg, qa	-876.734651	-876.733706	-876.795036	129.078000
ATCh(H_2O),gg, qa3m	-876.734627	-876.733683	-876.796378	131.952000
ATCh(H_2O),gt, br	-876.734376	-876.733432	-876.793666	126.772000
ATCh(H_2O),gt, qa	-876.731166	-876.730222	-876.793403	132.977000
ATCh(H_2O),tg, br	-876.739037	-876.738093	-876.798159	126.420000
ATCh(H_2O),tg, qa	-876.739755	-876.738811	-876.801498	131.937000
ATCh(H_2O),tg, qa3m	-876.739844	-876.738900	-876.801820	132.425000
ATCh(H_2O),tt, br	-876.737092	-876.736147	-876.796784	127.621000
ATCh(H_2O),tt, qa	-876.733706	-876.732762	-876.797418	136.081000
ATCh(H_2O),tt, qa3m	-876.733728	-876.732783	-876.797571	136.356000
ATCh(C_6H_6),gg', qa	-1031.336012	-1031.335067	-1031.406785	150.942000
ATCh(C_6H_6),gg', qa3m	-1031.336089	-1031.335144	-1031.407242	151.743000
ATCh(C_6H_6),gg, qa	-1031.335090	-1031.334145	-1031.407592	154.581000
ATCh(C_6H_6),gg, qa3m	-1031.334968	-1031.334024	-1031.407236	154.089000
ATCh(C_6H_6),tg, qa	-1031.340325	-1031.339381	-1031.413036	155.020000
ATCh(C_6H_6),tg, qa3m	-1031.340208	-1031.339264	-1031.412766	154.699000
ATCh(C_6H_6),tt, qa	-1031.333968	-1031.333024	-1031.408986	159.876000
ATCh(C_6H_6),tt, qa3m	-1031.333975	-1031.333030	-1031.408689	159.237000
ATCh(C_6H_6)(H_2O),gg', qa, qa3m	-1107.332588	-1107.331644	-1107.413886	173.093000
ATCh(C_6H_6)(H_2O),gg', qa3m, qa	-1107.332683	-1107.331738	-1107.414142	173.433000
ATCh(C_6H_6)(H_2O),gg, qa, br	-1107.333792	-1107.332848	-1107.413883	170.554000
ATCh(C_6H_6)(H_2O),gg, qa, qa3m	-1107.332060	-1107.331116	-1107.415537	177.679000
ATCh(C_6H_6)(H_2O),gg, qa3m, br	-1107.331537	-1107.330593	-1107.412272	171.908000
ATCh(C_6H_6)(H_2O),gg, qa3m, qa	-1107.332021	-1107.331076	-1107.414720	176.043000
ATCh(C_6H_6)(H_2O),gt, qa, qa3m	-1107.328089	-1107.327145	-1107.413158	181.030000
ATCh(C_6H_6)(H_2O),tg, qa, qa3m	-1107.337172	-1107.336227	-1107.420415	177.189000
ATCh(C_6H_6)(H_2O),tg, qa3m, qa	-1107.336979	-1107.336035	-1107.420119	176.969000
ATCh(C_6H_6)(H_2O),tt, qa3m, qa	-1107.331304	-1107.330360	-1107.416481	181.258000
C_6H_6	-230.591368	-230.590424	-230.620439	63.173000
H_2O	-75.984936	-75.983992	-76.005367	44.987000

[a]Energies in hartrees (au).
[b]Entropies in J/(mol·K).

Table 16. MP2/6-31G(d)Thermochemical Values at 298 K

Molecule	Energy[a]	Enthalpy[a]	Gibbs free energy[a]	Entropy[b]
ATCh,gg'	-802.117077	-802.116133	-802.166893	106.834000
ATCh,gg	-802.113726	-802.112782	-802.164892	109.676000
ATCh,tg	-802.118698	-802.117754	-802.170109	110.191000
ATCh,tt	-802.110620	-802.109675	-802.164323	115.016000
ATCh(H_2O),gg', br	-878.302917	-878.301972	-878.361714	125.737000
ATCh(H_2O),gg', qa	-878.303604	-878.302660	-878.363924	128.941000
ATCh(H_2O),gg', qa3m	-878.303436	-878.302492	-878.363556	128.519000
ATCh(H_2O),gg, br	-878.303711	-878.302767	-878.362315	125.329000
ATCh(H_2O),gg, qa	-878.301202	-878.300257	-878.361587	129.078000
ATCh(H_2O),gg, qa3m	-878.300681	-878.299737	-878.362432	131.952000
ATCh(H_2O),gt, br	-878.301554	-878.300610	-878.360844	126.772000
ATCh(H_2O),gt, qa	-878.297131	-878.296187	-878.359368	132.977000
ATCh(H_2O),tg, br	-878.305523	-878.304579	-878.364645	126.420000
ATCh(H_2O),tg, qa	-878.305372	-878.304428	-878.367115	131.937000
ATCh(H_2O),tg, qa3m	-878.305393	-878.304449	-878.367369	132.425000
ATCh(H_2O),tt, br	-878.303389	-878.302444	-878.363081	127.621000
ATCh(H_2O),tt, qa	-878.298011	-878.297067	-878.361723	136.081000
ATCh(H_2O),tt, qa3m	-878.297902	-878.296957	-878.361745	136.356000
ATCh(C_6H_6),gg', qa	-1033.473880	-1033.472935	-1033.544653	150.942000
ATCh(C_6H_6),gg', qa3m	-1033.473179	-1033.472234	-1033.544332	151.743000
ATCh(C_6H_6),gg, qa	-1033.470914	-1033.469969	-1033.543416	154.581000
ATCh(C_6H_6),gg, qa3m	-1033.470235	-1033.469291	-1033.542503	154.089000
ATCh(C_6H_6),tg, qa	-1033.476250	-1033.475306	-1033.548961	155.020000
ATCh(C_6H_6),tg, qa3m	-1033.475045	-1033.474101	-1033.547603	154.699000
ATCh(C_6H_6),tt, qa	-1033.468407	-1033.467463	-1033.543425	159.876000
ATCh(C_6H_6),tt, qa3m	-1033.467472	-1033.466527	-1033.542186	159.237000
ATCh(C_6H_6)(H_2O),gg', qa, qa3m	-1109.659012	-1109.658068	-1109.740310	173.093000
ATCh(C_6H_6)(H_2O),gg', qa3m, qa	-1109.658552	-1109.657607	-1109.740011	173.433000
ATCh(C_6H_6)(H_2O),gg, qa, br	-1109.660069	-1109.659125	-1109.740160	170.554000
ATCh(C_6H_6)(H_2O),gg, qa, qa3m	-1109.656531	-1109.655587	-1109.740008	177.679000
ATCh(C_6H_6)(H_2O),gg, qa3m, br	-1109.655532	-1109.654588	-1109.736267	171.908000
ATCh(C_6H_6)(H_2O),gg, qa3m, qa	-1109.655860	-1109.654915	-1109.738559	176.043000
ATCh(C_6H_6)(H_2O),gt, qa, qa3m	-1109.652362	-1109.651418	-1109.737431	181.030000
ATCh(C_6H_6)(H_2O),tg, qa, qa3m	-1109.661630	-1109.660685	-1109.744873	177.189000
ATCh(C_6H_6)(H_2O),tg, qa3m, qa	-1109.660303	-1109.659359	-1109.743443	176.969000
ATCh(C_6H_6)(H_2O),tt, qa3m, qa	-1109.653406	-1109.652462	-1109.738583	181.258000
C_6H_6	-231.344736	-231.343792	-231.373807	63.173000
H_2O	-76.170147	-76.169203	-76.190578	44.987000

[a]Energies in hartrees (au).
[b]Entropies in J/(mol·K).

Table 17. MP2/6-31+G(d) Thermochemical Values at 298 K

Molecule	Energy[a]	Enthalpy[a]	Gibbs free energy[a]	Entropy[b]
ATCh,gg'	-802.137272	-802.136328	-802.187088	106.834000
ATCh,gg	-802.134071	-802.133127	-802.185237	109.676000
ATCh,tg	-802.139271	-802.138327	-802.190682	110.191000
ATCh,tt	-802.130847	-802.129902	-802.184550	115.016000
ATCh(H_2O),gg', br	-878.335008	-878.334063	-878.393805	125.737000
ATCh(H_2O),gg', qa	-878.335244	-878.334300	-878.395564	128.941000
ATCh(H_2O),gg', qa3m	-878.334852	-878.333908	-878.394972	128.519000
ATCh(H_2O),gg, br	-878.336163	-878.335219	-878.394767	125.329000
ATCh(H_2O),gg, qa	-878.332939	-878.331994	-878.393324	129.078000
ATCh(H_2O),gg, qa3m	-878.332072	-878.331128	-878.393823	131.952000
ATCh(H_2O),gt, br	-878.334148	-878.333204	-878.393438	126.772000
ATCh(H_2O),gt, qa	-878.329021	-878.328077	-878.391258	132.977000
ATCh(H_2O),tg, br	-878.338319	-878.337375	-878.397441	126.420000
ATCh(H_2O),tg, qa	-878.337503	-878.336559	-878.399246	131.937000
ATCh(H_2O),tg, qa3m	-878.337083	-878.336139	-878.399059	132.425000
ATCh(H_2O),tt, br	-878.334826	-878.333881	-878.394518	127.621000
ATCh(H_2O),tt, qa	-878.329856	-878.328912	-878.393568	136.081000
ATCh(H_2O),tt, qa3m	-878.329241	-878.328296	-878.393084	136.356000
ATCh(C_6H_6),gg', qa	-1033.510015	-1033.509070	-1033.580788	150.942000
ATCh(C_6H_6),gg', qa3m	-1033.508602	-1033.507657	-1033.579755	151.743000
ATCh(C_6H_6),gg, qa	-1033.507497	-1033.506552	-1033.579999	154.581000
ATCh(C_6H_6),gg, qa3m	-1033.505641	-1033.504697	-1033.577909	154.089000
ATCh(C_6H_6),tg, qa	-1033.513233	-1033.512289	-1033.585944	155.020000
ATCh(C_6H_6),tg, qa3m	-1033.510558	-1033.509614	-1033.583116	154.699000
ATCh(C_6H_6),tt, qa	-1033.504782	-1033.503838	-1033.579800	159.876000
ATCh(C_6H_6),tt, qa3m	-1033.502653	-1033.501708	-1033.577367	159.237000
ATCh(C_6H_6)(H_2O),gg', qa, qa3m	-1109.706640	-1109.705696	-1109.787938	173.093000
ATCh(C_6H_6)(H_2O),gg', qa3m, qa	-1109.705800	-1109.704855	-1109.787259	173.433000
ATCh(C_6H_6)(H_2O),gg, qa, br	-1109.709378	-1109.708434	-1109.789469	170.554000
ATCh(C_6H_6)(H_2O),gg, qa, qa3m	-1109.704762	-1109.703818	-1109.788239	177.679000
ATCh(C_6H_6)(H_2O),gg, qa3m, br	-1109.703907	-1109.702963	-1109.784642	171.908000
ATCh(C_6H_6)(H_2O),gg, qa3m, qa	-1109.703090	-1109.702145	-1109.785789	176.043000
ATCh(C_6H_6)(H_2O),gt, qa, qa3m	-1109.700058	-1109.699114	-1109.785127	181.030000
ATCh(C_6H_6)(H_2O),tg, qa, qa3m	-1109.709995	-1109.709050	-1109.793238	177.189000
ATCh(C_6H_6)(H_2O),tg, qa3m, qa	-1109.707670	-1109.706726	-1109.790810	176.969000
ATCh(C_6H_6)(H_2O),tt, qa3m, qa	-1109.700499	-1109.699555	-1109.785676	181.258000
C_6H_6	-231.358622	-231.357678	-231.387693	63.173000
H_2O	-76.182889	-76.181945	-76.203320	44.987000

[a]Energies in hartrees (au).
[b]Entropies in J/(mol·K).

Table 18. HF/6-31G(d) Relative Thermochemical Values[a]

Molecule	ΔE_T	$\Delta H°$	$\Delta G°$	$\Delta S°$
ATCh,gg'	10.0	10.0	14.2	0.0
ATCh,gg	14.0	14.0	14.6	2.8
ATCh,tg	0.0	0.0	0.0	3.4
ATCh,tt	17.4	17.4	11.4	8.2
ATCh(H_2O),gg', br	13.2	13.2	21.5	0.4
ATCh(H_2O),gg', qa	10.6	10.6	15.0	3.6
ATCh(H_2O),gg', qa3m	10.9	10.9	15.8	3.2
ATCh(H_2O),gg, br	9.6	9.6	18.4	0.0
ATCh(H_2O),gg, qa	13.6	13.6	17.8	3.7
ATCh(H_2O),gg, qa3m	13.7	13.7	14.3	6.6
ATCh(H_2O),gt, br	14.4	14.4	21.4	1.4
ATCh(H_2O),gt, qa	22.8	22.8	22.1	7.6
ATCh(H_2O),tg, br	2.1	2.1	9.6	1.1
ATCh(H_2O),tg, qa	0.2	0.2	0.8	6.6
ATCh(H_2O),tg, qa3m	0.0	0.0	0.0	7.1
ATCh(H_2O),tt, br	7.2	7.2	13.2	2.3
ATCh(H_2O),tt, qa	16.1	16.1	11.6	10.8
ATCh(H_2O),tt, qa3m	16.1	16.1	11.2	11.0
ATCh(C_6H_6),gg', qa	11.3	11.3	16.4	0.0
ATCh(C_6H_6),gg', qa3m	11.1	11.1	15.2	0.8
ATCh(C_6H_6),gg, qa	13.7	13.7	14.3	3.6
ATCh(C_6H_6),gg, qa3m	14.1	14.1	15.2	3.1
ATCh(C_6H_6),tg, qa	0.0	0.0	0.0	4.1
ATCh(C_6H_6),tg, qa3m	0.3	0.3	0.7	3.8
ATCh(C_6H_6),tt, qa	16.7	16.7	10.6	8.9
ATCh(C_6H_6),tt, qa3m	16.7	16.7	11.4	8.3
ATCh(C_6H_6)(H_2O),gg', qa, qa3m	12.0	12.0	17.1	2.5
ATCh(C_6H_6)(H_2O),gg', qa3m, qa	11.8	11.8	16.5	2.9
ATCh(C_6H_6)(H_2O),gg, qa, br	8.9	8.9	17.2	0.0
ATCh(C_6H_6)(H_2O),gg, qa, qa3m	13.4	13.4	12.8	7.1
ATCh(C_6H_6)(H_2O),gg, qa3m, br	14.8	14.8	21.4	1.4
ATCh(C_6H_6)(H_2O),gg, qa3m, qa	13.5	13.5	15.0	5.5
ATCh(C_6H_6)(H_2O),gt, qa, qa3m	23.8	23.8	19.1	10.5
ATCh(C_6H_6)(H_2O),tg, qa, qa3m	0.0	0.0	0.0	6.6
ATCh(C_6H_6)(H_2O),tg, qa3m, qa	0.5	0.5	0.8	6.4
ATCh(C_6H_6)(H_2O),tt, qa3m, qa	15.4	15.4	10.3	10.7

[a] ΔE_T, $\Delta H°$ and $\Delta G°$ in kJ/mol, $\Delta S°$ in J/(mol·K), at 298K.

Table 19. MP2/6-31G(d) Relative Thermochemical Values[a]

Molecule	ΔE_T	$\Delta H°$	$\Delta G°$	$\Delta S°$
ATCh,gg'	4.3	4.3	8.4	0.0
ATCh,gg	13.1	13.1	13.7	2.8
ATCh,tg	0.0	0.0	0.0	3.4
ATCh,tt	21.2	21.2	15.2	8.2
ATCh(H_2O),gg', br	6.8	6.8	14.8	0.4
ATCh(H_2O),gg', qa	5.0	5.0	9.0	3.6
ATCh(H_2O),gg', qa3m	5.5	5.5	10.0	3.2
ATCh(H_2O),gg, br	4.8	4.8	13.3	0.0
ATCh(H_2O),gg, qa	11.3	11.3	15.2	3.7
ATCh(H_2O),gg, qa3m	12.7	12.7	13.0	6.6
ATCh(H_2O),gt, br	10.4	10.4	17.1	1.4
ATCh(H_2O),gt, qa	22.0	22.0	21.0	7.6
ATCh(H_2O),tg, br	0.0	0.0	7.2	1.1
ATCh(H_2O),tg, qa	0.4	0.4	0.7	6.6
ATCh(H_2O),tg, qa3m	0.3	0.3	0.0	7.1
ATCh(H_2O),tt, br	5.6	5.6	11.3	2.3
ATCh(H_2O),tt, qa	19.7	19.7	14.8	10.8
ATCh(H_2O),tt, qa3m	20.0	20.0	14.8	11.0
ATCh(C_6H_6),gg', qa	6.2	6.2	11.3	0.0
ATCh(C_6H_6),gg', qa3m	8.1	8.1	12.2	0.8
ATCh(C_6H_6),gg, qa	14.0	14.0	14.6	3.6
ATCh(C_6H_6),gg, qa3m	15.8	15.8	17.0	3.1
ATCh(C_6H_6),tg, qa	0.0	0.0	0.0	4.1
ATCh(C_6H_6),tg, qa3m	3.2	3.2	3.6	3.8
ATCh(C_6H_6),tt, qa	20.6	20.6	14.5	8.9
ATCh(C_6H_6),tt, qa3m	23.0	23.1	17.8	8.3
ATCh(C_6H_6)(H_2O),gg', qa, qa3m	6.9	6.9	12.0	2.5
ATCh(C_6H_6)(H_2O),gg', qa3m, qa	8.1	8.1	12.8	2.9
ATCh(C_6H_6)(H_2O),gg, qa, br	4.1	4.1	12.4	0.0
ATCh(C_6H_6)(H_2O),gg, qa, qa3m	13.4	13.4	12.8	7.1
ATCh(C_6H_6)(H_2O),gg, qa3m, br	16.0	16.0	22.6	1.4
ATCh(C_6H_6)(H_2O),gg, qa3m, qa	15.1	15.1	16.6	5.5
ATCh(C_6H_6)(H_2O),gt, qa, qa3m	24.3	24.3	19.5	10.5
ATCh(C_6H_6)(H_2O),tg, qa, qa3m	0.0	0.0	0.0	6.6
ATCh(C_6H_6)(H_2O),tg, qa3m, qa	3.5	3.5	3.8	6.4
ATCh(C_6H_6)(H_2O),tt, qa3m, qa	21.6	21.6	16.5	10.7

[a] ΔE_T, $\Delta H°$ and $\Delta G°$ in kJ/mol, $\Delta S°$ in J/(mol·K) at 298K.

Table 20. MP2/6-31+G(d) Relative Thermochemical Values[a]

Molecule	ΔE_T	$\Delta H°$	$\Delta G°$	$\Delta S°$
ATCh,gg'	5.2	5.2	9.4	0.0
ATCh,gg	13.7	13.6	14.3	2.8
ATCh,tg	0.0	0.0	0.0	3.4
ATCh,tt	22.1	22.1	16.1	8.2
ATCh(H_2O),gg', br	8.7	8.7	14.3	0.4
ATCh(H_2O),gg', qa	8.1	8.1	9.7	3.6
ATCh(H_2O),gg', qa3m	9.1	9.1	11.2	3.2
ATCh(H_2O),gg, br	5.7	5.7	11.8	0.0
ATCh(H_2O),gg, qa	14.1	14.1	15.5	3.7
ATCh(H_2O),gg, qa3m	16.4	16.4	14.2	6.6
ATCh(H_2O),gt, br	11.0	11.0	15.2	1.4
ATCh(H_2O),gt, qa	24.4	24.4	21.0	7.6
ATCh(H_2O),tg, br	0.0	0.0	4.7	1.1
ATCh(H_2O),tg, qa	2.1	2.1	0.0	6.6
ATCh(H_2O),tg, qa3m	3.2	3.2	0.5	7.1
ATCh(H_2O),tt, br	9.2	9.2	12.4	2.3
ATCh(H_2O),tt, qa	22.2	22.2	14.9	10.8
ATCh(H_2O),tt, qa3m	23.8	23.8	16.2	11.0
ATCh(C_6H_6),gg', qa	8.4	8.5	13.5	0.0
ATCh(C_6H_6),gg', qa3m	12.2	12.2	16.2	0.8
ATCh(C_6H_6),gg, qa	15.1	15.1	15.6	3.6
ATCh(C_6H_6),gg, qa3m	19.9	19.9	21.1	3.1
ATCh(C_6H_6),tg, qa	0.0	0.0	0.0	4.1
ATCh(C_6H_6),tg, qa3m	7.0	7.0	7.4	3.8
ATCh(C_6H_6),tt, qa	22.2	22.2	16.1	8.9
ATCh(C_6H_6),tt, qa3m	27.8	27.8	22.5	8.3
ATCh(C_6H_6)(H_2O),gg', qa, qa3m	8.8	8.8	13.9	2.5
ATCh(C_6H_6)(H_2O),gg', qa3m, qa	11.0	11.0	15.7	2.9
ATCh(C_6H_6)(H_2O),gg, qa, br	1.6	1.6	9.9	0.0
ATCh(C_6H_6)(H_2O),gg, qa, qa3m	13.7	13.7	13.1	7.1
ATCh(C_6H_6)(H_2O),gg, qa3m, br	16.0	16.0	22.6	1.4
ATCh(C_6H_6)(H_2O),gg, qa3m, qa	18.1	18.1	19.6	5.5
ATCh(C_6H_6)(H_2O),gt, qa, qa3m	26.1	26.1	21.3	10.5
ATCh(C_6H_6)(H_2O),tg, qa, qa3m	0.0	0.0	0.0	6.6
ATCh(C_6H_6)(H_2O),tg, qa3m, qa	6.1	6.1	6.4	6.4
ATCh(C_6H_6)(H_2O),tt, qa3m, qa	24.9	24.9	19.9	10.7

[a] ΔE_T, $\Delta H°$ and $\Delta G°$ in kJ/mol, $\Delta S°$ in J/(mol·K) at 298K.

Table 21. HF/6-31G(d) Thermochemistry of Association Reactions[a]

Reactions[b]	$-\Delta H°_{rx}$	$-\Delta S°_{rx}$	$-\Delta G°_{rx}$
ATCh + $H_2O \rightarrow$ ATCh(H_2O)	36.5	22.8	8.1
ATCh(C_6H_6) + $H_2O \rightarrow$ ATCh(C_6H_6)(H_2O)	33.7	22.8	5.3
ATCh + $C_6H_6 \rightarrow$ ATCh(C_6H_6)	20.9	18.3	-2.0
ATCh(H_2O) + $C_6H_6 \rightarrow$ ATCh(C_6H_6)(H_2O)	18.1	18.4	-4.8

[a] $\Delta H°_{rx}$ and $\Delta G°_{rx}$ in kJ/mol, $\Delta S°_{rx}$ in J/(mol·K) at 298K.
[b] Molecules used here are: ATCh, tg, ATCh(H_2O), tg, qa3m, ATCh(C_6H_6), tg, qa and ATCh(C_6H_6)(H_2O), tg, qa, qa3m.

Table 22. MP2/6-31G(d) Thermochemistry of Association Reactions[a]

Reactions[b]	$-\Delta H°$	$-\Delta S°$	$-\Delta G°$
ATCh + $H_2O \rightarrow$ ATCh(H_2O)	45.9	22.8	17.5
ATCh(C_6H_6) + $H_2O \rightarrow$ ATCh(C_6H_6)(H_2O)	42.5	22.8	14.0
ATCh + $C_6H_6 \rightarrow$ ATCh(C_6H_6)	36.1	18.3	13.2
ATCh(H2O) + $C_6H_6 \rightarrow$ ATCh(C_6H_6)(H_2O)	32.7	18.4	9.7

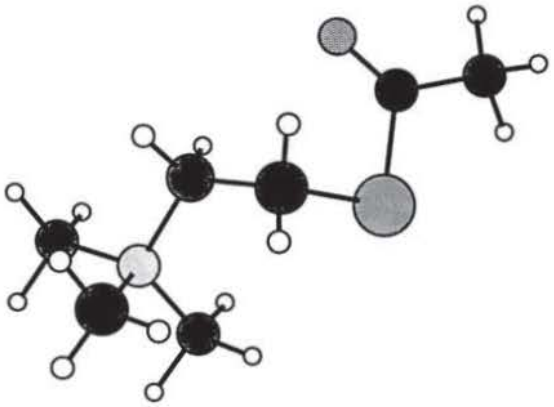
[a] $\Delta H°_{rx}$ and $\Delta G°_{rx}$ in kJ/mol, $\Delta S°_{rx}$ in J/(mol·K) at 298K.
[b] Molecules used here are: ATCh, tg, ATCh(H_2O), tg, qa3m, ATCh(C_6H_6), tg, qa and ATCh(C_6H_6)(H_2O), tg, qa, qa3m.

Table 23. MP2/6-31+G(d) Thermochemistry of Association Reactions[a]

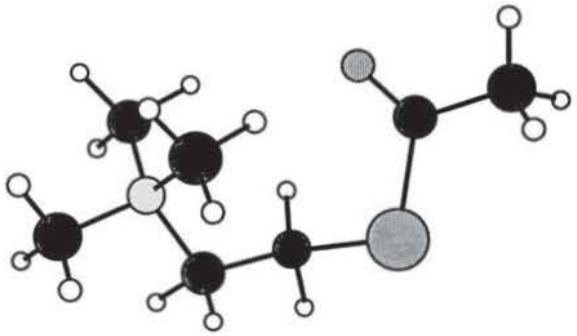
Reactions[b]	$-\Delta H°$	$-\Delta S°$	$-\Delta G°$
ATCh + $H_2O \rightarrow$ ATCh(H_2O)	42.8	23.2	13.8
ATCh(C_6H_6) + $H_2O \rightarrow$ ATCh(C_6H_6)(H_2O)	38.9	22.8	10.4
ATCh + $C_6H_6 \rightarrow$ ATCh(C_6H_6)	42.8	18.3	19.9
ATCh(H2O) + $C_6H_6 \rightarrow$ ATCh(C_6H_6)(H_2O)	38.9	17.9	16.5

[a] $\Delta H°_{rx}$ and $\Delta G°_{rx}$ in kJ/mol, $\Delta S°_{rx}$ in J/(mol·K) at 298K.
[b] Molecules used here are: ATCh, tg, ATCh(H_2O), tg, qa, ATCh(C_6H_6), tg, qa and ATCh(C_6H_6)(H_2O), tg, qa, qa3m.

Figure 1. Structures of ATCh



ATCh, gg



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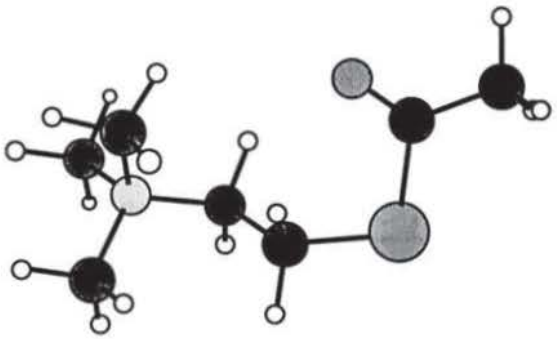

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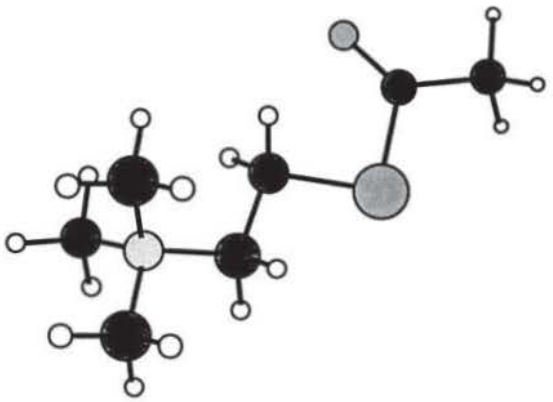
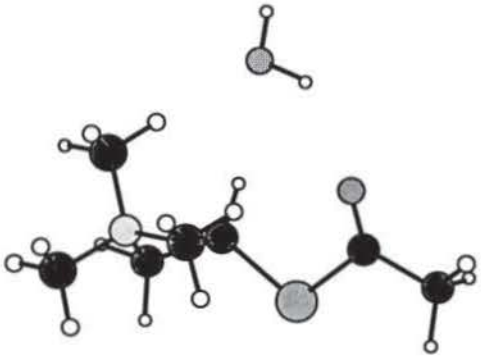
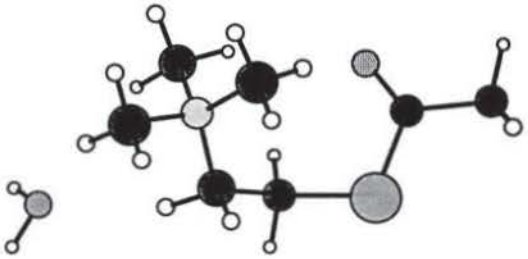


ATCh, tt

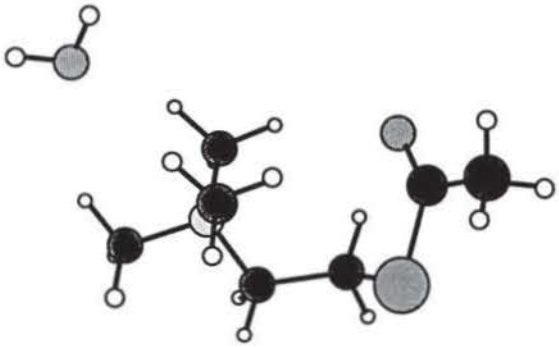
Figure 2. Structures of ATCh(H_2O)



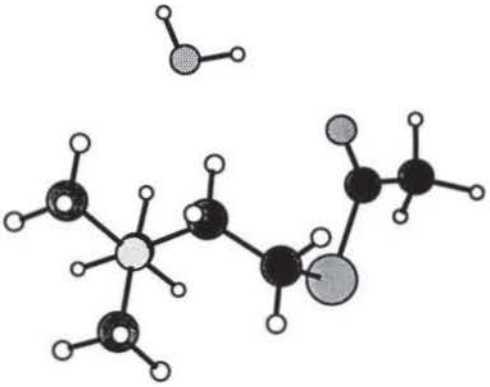
ATCh(H_2O), gg', br



ATCh(H_2O), gg', qa

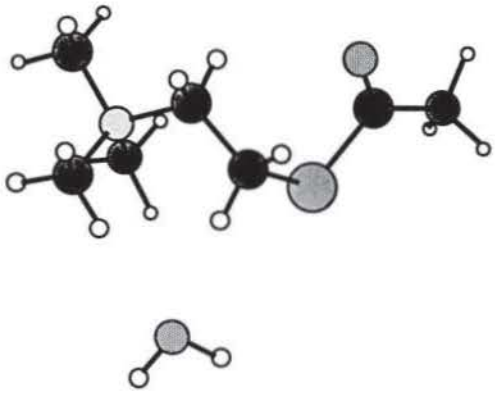


ATCh(H_2O), gg', qa3m

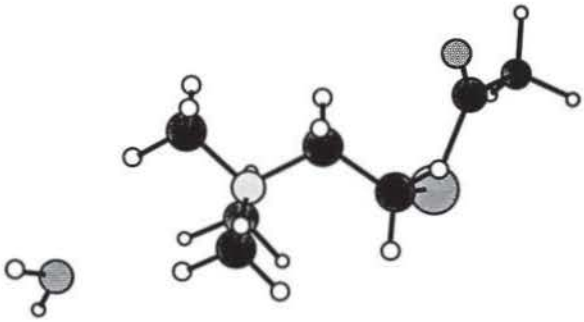


ATCh(H_2O), gg', br

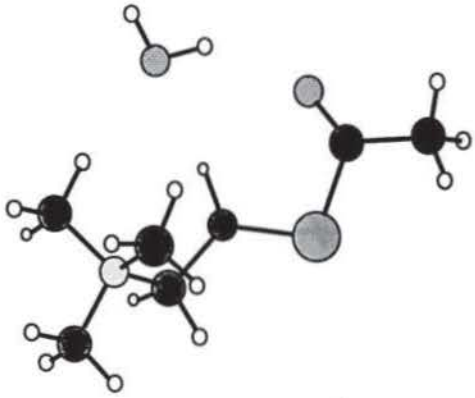
Figure 2. Structures of ATCh(H_2O) (cont'd.)



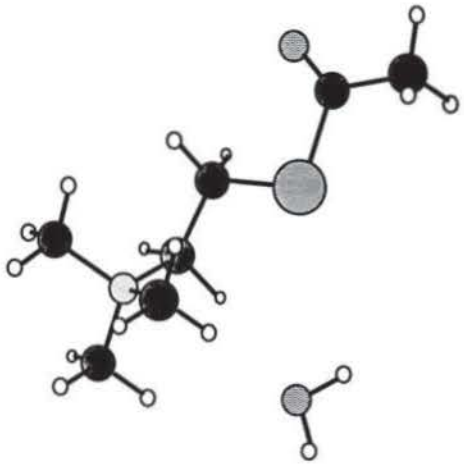
ATCh(H_2O), gg, qa



ATCh(H_2O), gg, qa3m

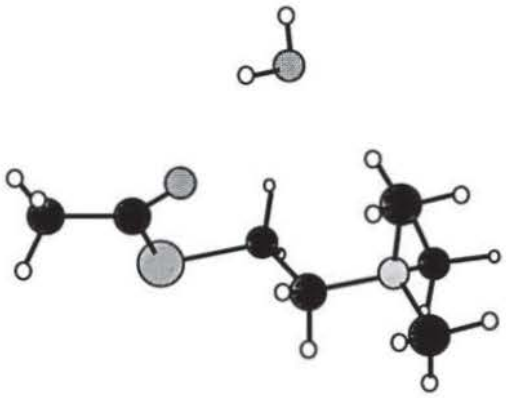


ATCh(H_2O), gt, br

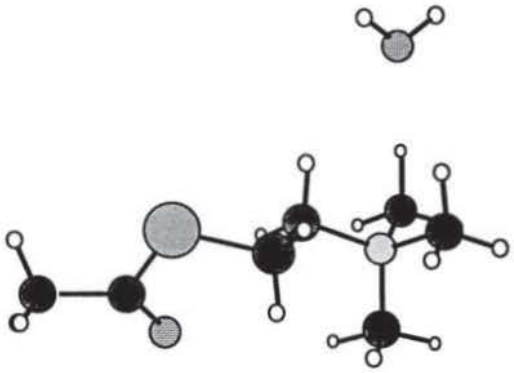


ATCh(H_2O), gt, qa

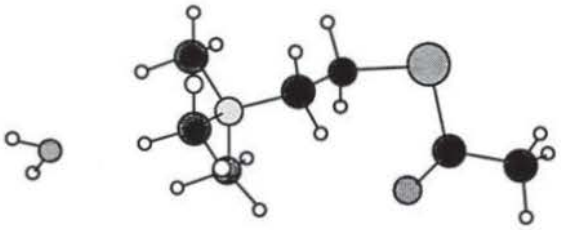
Figure 2. Structures of ATCh(H_2O) (cont'd.)



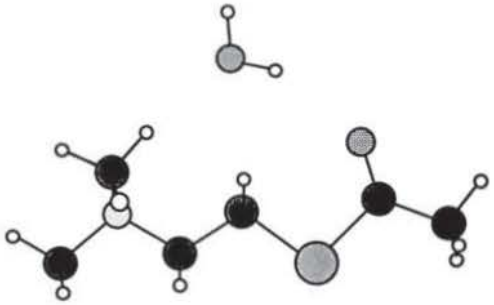
ATCh(H_2O), tg, br



ATCh(H_2O), tg, qa

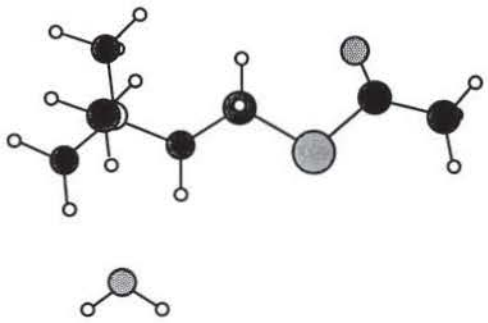


ATCh(H_2O), tg, qa3m

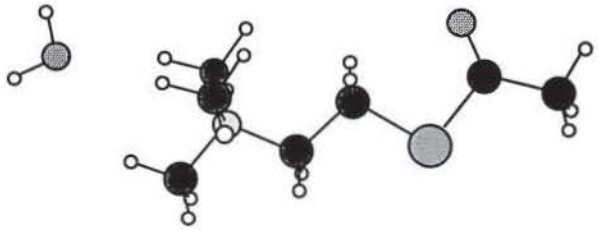


ATCh(H_2O), tt, br

Figure 2. Structures of ATCh(H_2O) (cont'd.)

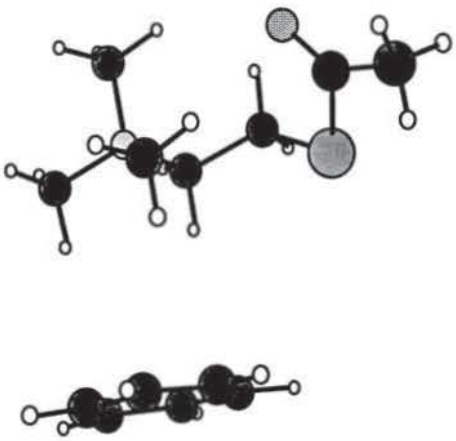


ATCh(H_2O), tt, qa

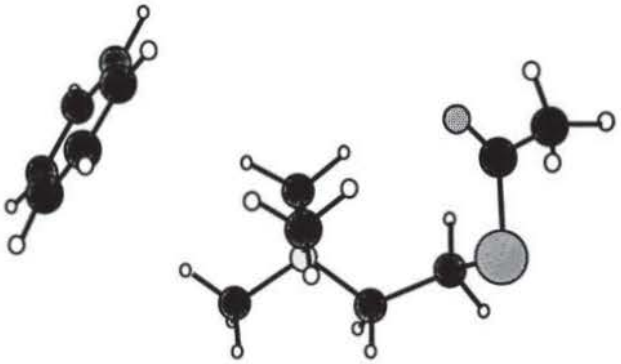


ATCh(H_2O), tt, qa3m

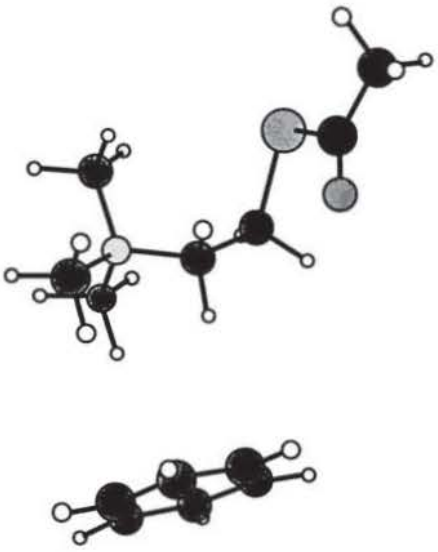
Figure 3. Structures of ATCh(C_6H_6)



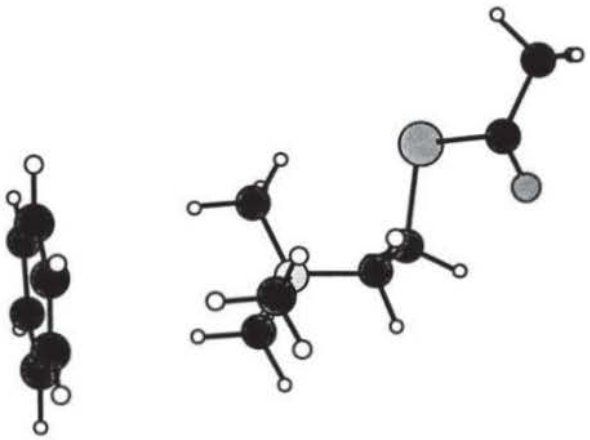
ATCh(C_6H_6), gg', qa



ATCh(C_6H_6), gg', qa3m

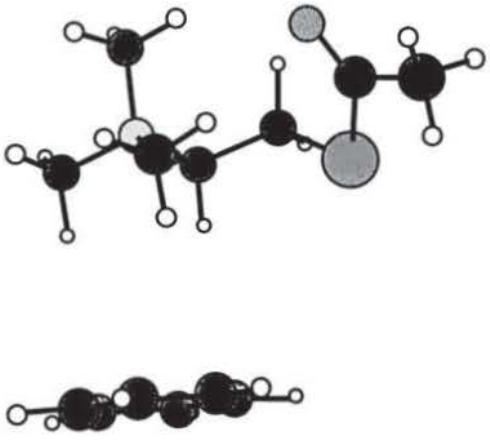


ATCh(C_6H_6), gg, qa

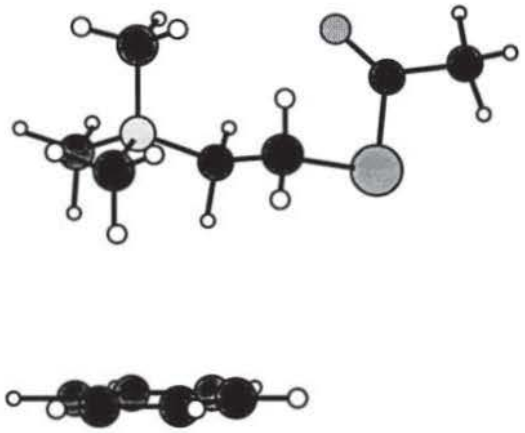


ATCh(C_6H_6), gg, qa3m

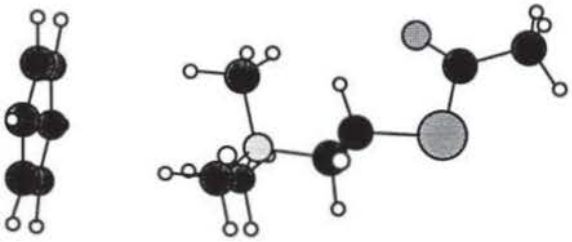
Figure 3. Structures of ATCh(C_6H_6) (cont'd.)



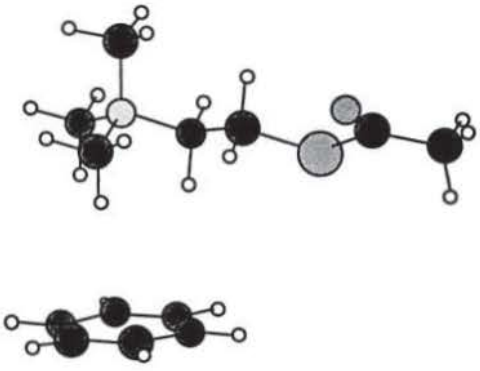
ATCh(C_6H_6), gt, qa



ATCh(C_6H_6), tg, qa

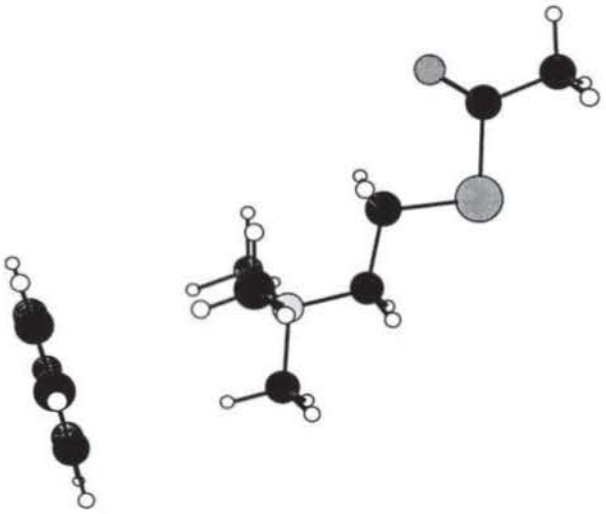


ATCh(C_6H_6), tg, qa3m



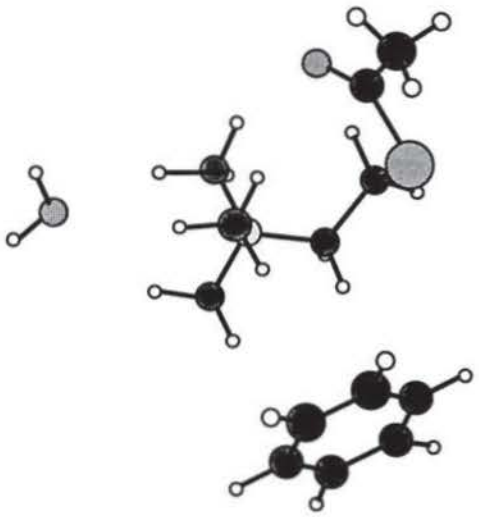
ATCh(C_6H_6), tt, qa

Figure 3. Structures of ATCh(C_6H_6) (cont'd.)

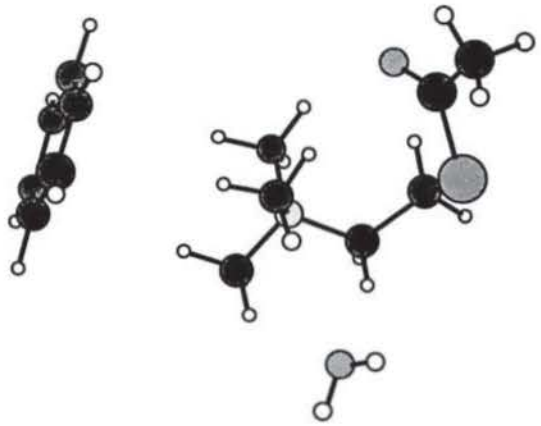


ATCh(C_6H_6), tt, qa3m

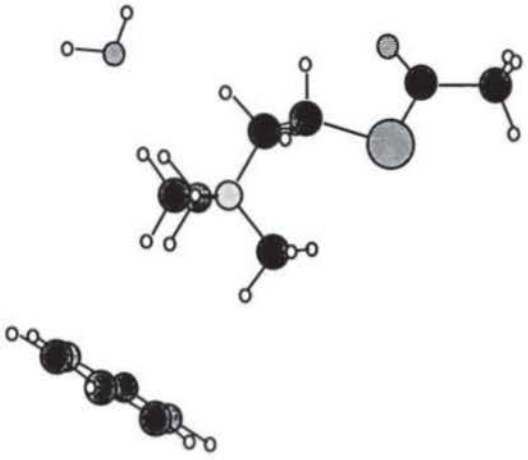
Figure 4. Structures of $ATCh(C_6H_6)(H_2O)$



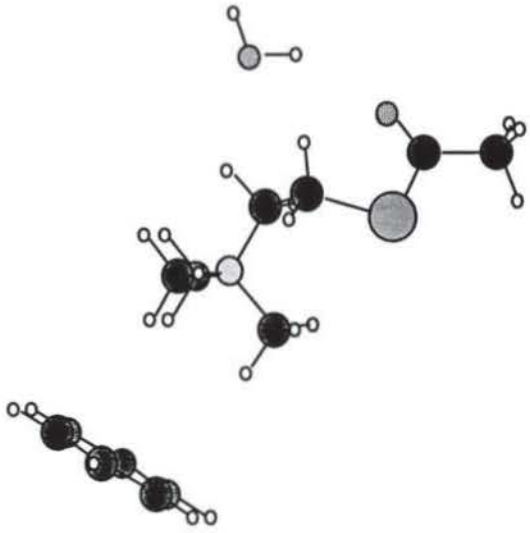
$ATCh(C_6H_6)(H_2O)$, gg', qa, qa3m



$ATCh(C_6H_6)(H_2O)$, gg', qa3m, qa

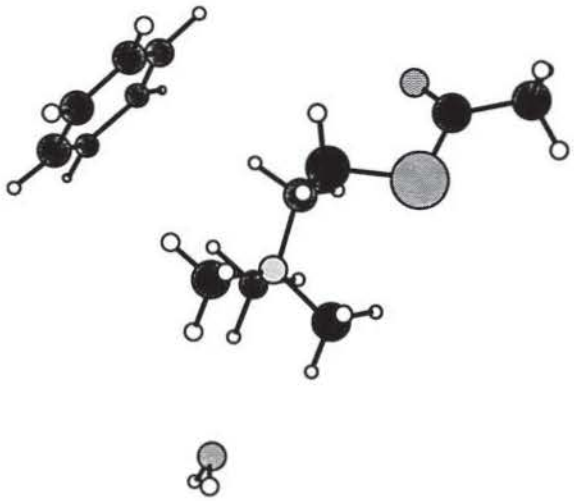


$ATCh(C_6H_6)(H_2O)$, gg, qa3m, qa

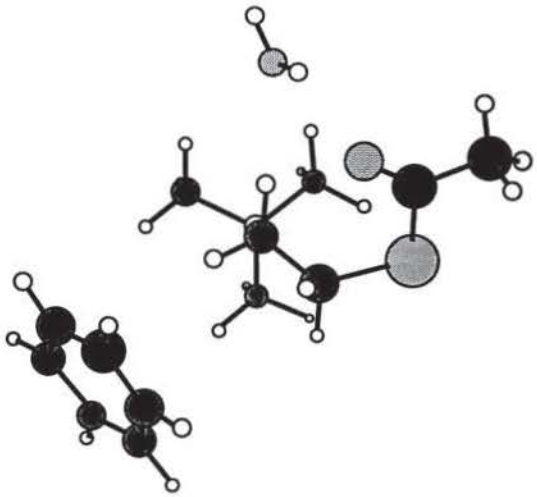


$ATCh(C_6H_6)(H_2O)$, gg, qa3m, br

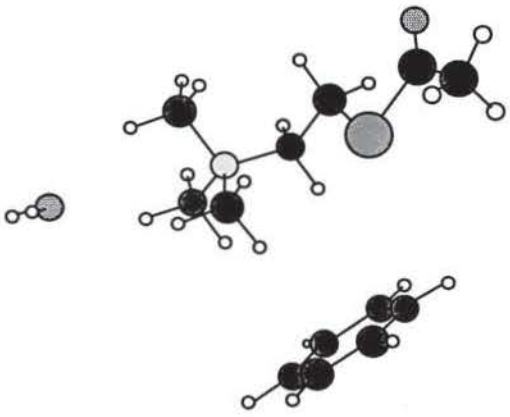
Figure 4. Structures of ATCh(C_6H_6)(H_2O) (cont'd.)



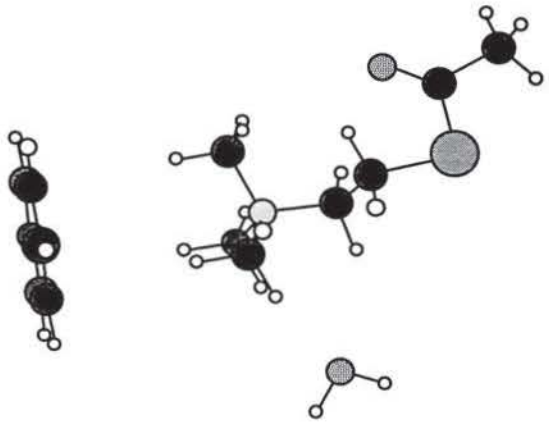
ATCh(C_6H_6)(H_2O), gg, qa, qa3m



ATCh(C_6H_6)(H_2O), gg, qa, br

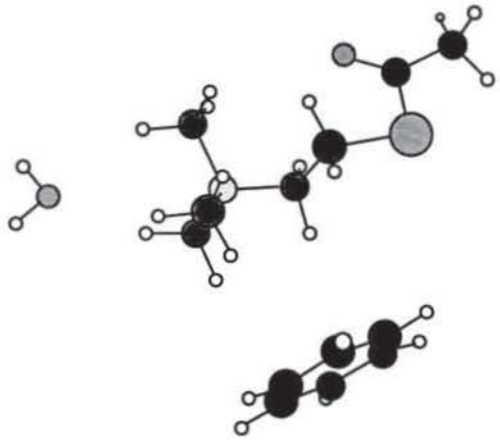


ATCh(C_6H_6)(H_2O), gt, qa, qa3m

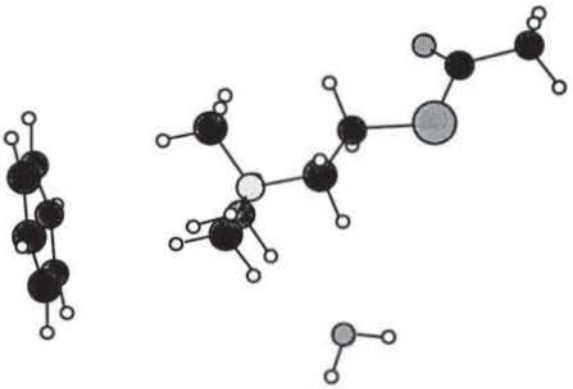


ATCh(C_6H_6)(H_2O), tg, qa3m, qa

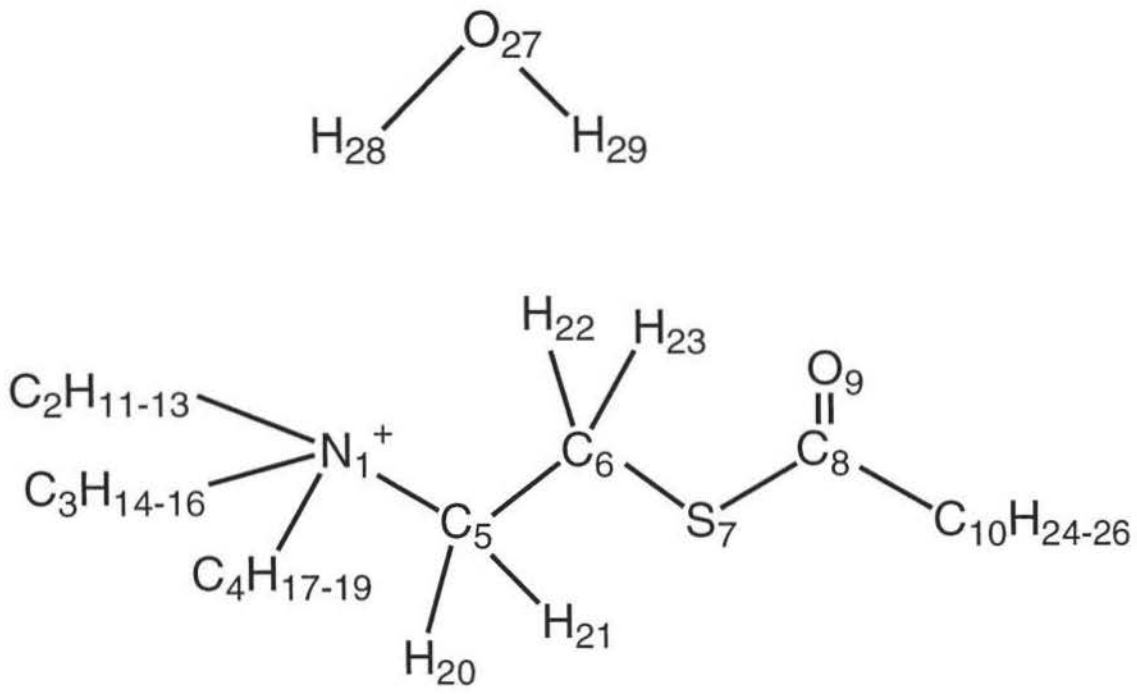
Figure 4. Structures of ATCh(C_6H_6)(H_2O) (cont'd.)



ATCh(C_6H_6)(H_2O), tg, qa, qa3m



ATCh(C_6H_6)(H_2O), tt, qa3m, qa


O27
H28
H29
H22
H23
O9
C2H11-13
N1+
C6
C8
C3H14-16
C5
S7
C10H24-26
C4H17-19
H21
H20

Scheme 1.